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THE UNIVERSITY OF ALBERTA

A STUDY OF DEHYDRATION AND AROMA RETENTION IN ONION

by

© G. Mazza

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled A Study of Dehydration and Aroma Retention in Onion

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ABSTRACT

The water vapor sorption isotherms of onion were determined for the temperature range $10 \leq T \leq 45$, and the water activity, $0.11 \leq a_w \leq 1.00$. B.E.T. monolayers, heat of sorption and surface areas were calculated from the isotherms. By using the surface areas obtained from the B.E.T. analysis an attempt was made to calculate thermodynamic functions such as molar entropy and equilibrium heat of sorption. Isosteric heat of the water adsorption and desorption were obtained by applying the Clausius-Clapeyron equation.

Dehydration experiments with onion slices were carried out in a Vibro Fluidizer with air at different temperatures and flow rates. Drying-rate curves were constructed and used for the calculation of heat and mass transfer coefficients, effective diffusivity of moisture through the slices, Biot number, and the parameters α and β, which determine the degree of internal and external mass or heat transfer control. Rehydration rates at 25 and 40°C were also determined and found to be independent of drying conditions. To relate the removal of moisture to the loss of volatiles, a method of analysis which was suitable for routine qualitative and quantitative determinations of the volatiles of fresh and processed onion was developed following a comparison of techniques for analyzing onion aroma. Volatile components in headspace were identified and analyzed by gas chromatography-mass spectrometry utilizing an on-column entrainment procedure.

The volatilities of propanethiol, 2,5-dimethylthiophene, methyl propyl sulfide, dimethyl disulfide, dipropyl disulfide, allyl methyl sulfide, diallyl sulfide, diallyl disulfide, ethanal, propanal,

methanol, ethanol, 1-propanol and 2-propanol in dilute water solutions were also studied experimentally by gas chromatography. The volatilities of these compounds varied appreciably. They were higher for thiols, thiophenes and monosulfides, than disulfides, aldehydes or alcohols. The results for aldehydes and alcohols confirmed earlier theoretical predictions by other authors that at 25°C the volatility in very dilute solution increases as the carbon chain gets longer.

The retention of four onion volatiles was then studied as a function of drying rate, location of the volatiles in the onion, and some physico-chemical properties of the components. It was shown that percent retention of propanethiol, methyl propyl disulfide, dipropyl disulfide and propanol is almost linearly related to moisture content with a break in the curve at different points depending on the compound examined and drying rate. Evidence is also presented that the quantity of aroma retained by dried onion slices is dependent on the initial concentration of the volatile, solids concentration and properties of the aroma compounds.

Intensification of aroma during rehydration of onion was also investigated by rehydrating samples with water and cysteine solutions. For this last aspect of the study, rehydration temperatures of 22 and 40°C, and four flavour development times were investigated. Samples rehydrated with cysteine solution generally gave less total volatiles when the development period was 15, 30 or 60 min, and more after 2 hours than water rehydrated samples. Propanal, propanol and propanethiol contents were always higher in samples rehydrated with water. The plausible reactions responsible for the observed effect of cysteine are discussed.

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LIST OF SYMBOLS

Symbol	Definition
A	Solid specific surface area, m^2/kg solid
A_{H_2O}	Area of water molecule, 10.6×10^{-20} m^2/molecule
a_w	Water activity (-)
B.E.T.	Brunauer, Emmet and Teller
B_i^*	Biot number (-)
C	Constant defined by equation (2.1)
C_2	Constant reflecting the geometry of the porous medium, $= \xi/\tau^2$, where ξ = voidage and τ^2 = tortuosity.
D	Binary diffusivity in the free gas, = 25.6 m^2/s at 25°C for H_2O - air.
D^1	Effective vapor space diffusion coefficient, m^2/S
D_{eff}	Effective diffusion coefficient, m^2/S
Fo	Fourier number (-)
h	External heat transfer coefficient, J/s m^2K
ha	Hectare
ΔH	Equilibrium heat of sorption defined by equation (2.4)
ΔH_s	Molar heat of sorption, J/kg mole
k	Thermal conductivity, w/mK
k_c	External mass transfer coefficient, m/s
k_c^*	Combined external heat and mass transfer coefficient defined by equation (3.3)
L	Characteristic piece dimension, m
M_{H_2O}	Molecular weight of water, 18 kg/kmole
N	Avagodro's number, 6.023×10^{26} molecules/kmole
N_w	Molar flux of water, kmole/m^2s

Symbol	Definition
P	Pressure, Pa
P_o	Vapor pressure of pure water at T, Pa
P_w	Water vapor pressure exerted by the food material, Pa
q_{st}	Isosteric heat of sorption defined by equation (2.3)
R	Gas constant, 0.46188 kJ/kg K or 8.3143×10^3 J/kmole K
R_v	Gas constant, 8.3143×10^3 J/kmole K
S_G	Entropy of water vapor at T, kJ/kg K
S_L	Molar entropy of liquid water, kJ/kg K
S_s	Molar entropy of adsorbed layer, kJ/kg K
ΔS	Molar integral entropy, kJ/kg K
T	Temperature ^oC or K
T_{DB}	Dry bulb temperature, ^oC
T_{WB}	Wet bulb temperature, ^oC
V	Volume of piece, m^3
v	Air velocity, m/s
w	Weight of sample, kg
X	Moisture content, kg H_2O/kg Dry Matter (D.M.)
X_c	Critical moisture content, kg H_2O/kg D.M.
X_e	Equilibrium moisture content, kg H_2O/kg D.M.
X_m	Monolayer moisture content, kg H_2O/kg D.M.
X_o	Moisture content of fresh onion, kg H_2O/kg D.M.
α	Defined by Equation (3.6)
α_{io}	Volatility of aroma component relative to water (-)
β	Defined by Equation (3.5)
θ	Time, min or h
Φ	Spreading pressure defined by Equation (2.5)

Symbol	Definition
Γ	Surface concentration, X/A, kg H_2O/m^2 solid
λ	Heat of vaporization of water, kJ/kg
ρ_e	Density of onion slices at X_e
H_2O	Density of water, 1 g/cm^2
ρ_L	Density of condensed phase, kg/m^3
ρ_s	Density of the solid with no moisture, kg/m^3
ρ_v	Density of vapor phase, kg/m^3

I. GENERAL INTRODUCTION

Onion (*Allium cepa* L.) has had a long and interesting history of use as a vegetable and spice. It probably originated in Western Asia and has been under cultivation for 5,000 or more years (Jones & Mann, 1963). The demand for onions is world-wide. Their use is not limited to any climate or associated with any nationality, and they are as widely grown as any cultivated crop. The leading onion producing countries are the United States, China, India, the Soviet Union, Japan, Spain, Turkey, Egypt, The Netherlands and Italy. World production in 1977 was 17.4 million tonnes, with a rather steady trend upward (Table 1). Europe produced 5.1 million tonnes; North America, 1.7; South America, 1.2; Asia, 7.9; Africa, 1.3; and Oceania, 0.15 (F.A.O., 1978).

Canadian onion production in 1977 was 117,482 tonnes, the second largest production ever. Table 2 shows crop data including acreage, yield, production, farm price and farm value from 1958 to 1978. Since the farm value was about 30% of the retail value, in 1977 the retail value was over $36 million. Canada is, however, a net importer of onions. Imports in 1977 were 57,102 tonnes of fresh onions, and 1,895 tonnes of dehydrated onion, worth over $16.4 million. In 1977, onion exports amounted to 9,692 tonnes with a value of $2.4 million. The net Canadian foreign trade deficit, resulting from the onion trade, was $14 million. Tables 3 and 4 show the quantity and value of Canadian onion imports and exports from 1973 to 1977. Canada receives onions mainly from the United States, New Zealand, Mexico, Spain and

Table 1. World onion area harvested, yield and production (F.A.O., 1978).

Year	Area (1,000 ha)	Yield (kg/ha)	Production (1,000 mt)
1961-65	1,085	10,791	11,703
1974	1,404	11,598	16,288
1975	1,412	11,119	15,705
1976	1,463	11,145	16,303
1977	1,525	11,408	17,399

Table 2. Canada onion acreage, production, farm price and value, 1958 -1978 (Statistics Canada, 1978a).

Year	Hectares	Yield (kg/ha)	Production (Tonnes)	Average farm price ($/kg)	Total farm value ($1,000)
1958	2,545	20,017	50,943	0.07	3,740
1959	2,930	21,695	63,568	0.06	3,533
1960	31,48	25,137	79,131	0.05	3,946
1961	3,242	21,613	70,069	0.08	5,755
1962	3,517	29,116	102,401	0.06	6,185
1963	3,889	29,376	114,248	0.05	5,638
1964	3,760	25,224	94,842	0.06	5,409
1965	3,978	31,675	125,999	0.04	4,903
1966	3,407	25,058	85,373	0.09	7,664
1967	3,561	25,098	89,374	0.07	6,578
1968	3,638	31,171	113,401	0.05	5,573
1969	3,594	25,867	92,966	0.09	8,368
1970	3,522	27,761	100,552	0.05	4,941
1971	3,505	29,410	103,083	0.06	6,590
1972	3,460	23,123	80,005	0.16	12,756
1973	3,634	26,088	94,805	0.12	11,014
1974	3,368	29,356	98,869	0.12	11,616
1975	3,352	29,845	100,040	0.16	16,036
1976	3,716	35,657	95,424	0.14	13,182
1977	3,649	32,169	117,982	0.09	10,959
1978	3,868	N/A	N/A	N/A	N/A

Table 3. Imports of fresh onion into Canada, 1973-1977 (Statistics Canada, 1978b).

Year	Quantity (1,000 kg)	Value ($1,000)
1973	41,756	8,772
1974	38,992	5,397
1975	43,988	10,531
1976	70,978	9,830
1977	57,102	13,627

Table 4. Exports of fresh onion out of Canada, 1973-1977 (Statistics Canada, 1978c).

	Domestic Exports		Re-exports	
Year	Quantity (1,000 kg)	Value ($1,000)	Quantity (1,000 kg)	Value ($1,000)
1973	12,797	3,057	402	151
1974	7,909	1,614	114	48
1975	13,220	2,522	-	-
1976	13,073	2,983	1,520	403
1977	9,625	2,320	57	37

Table 5. Per capita disappearance of onions, not processed, 1974-1977 (Statistics Canada, 1978d).

	Fresh equivalent	
Year	kilos/year	g/day
1974	5.67	15.53
1975	6.11	16.74
1976	6.27	17.17
1977	6.19	16.97

Australia; and exports to the United Kindom and the Caribbeans (Statistics Canada, 1978c). Per capita Canadian consumption of onion has remained relatively stable during recent years (Table 5), but population increases in the years ahead will require expansion of the industry to maintain imports at current levels.

Alberta is a minor producer of onions, with only 1.57% of Canada's total production in 1977. Table 6 shows Alberta onion acreage, production and farm value from 1965 to 1978. There has been interest in increasing onion production in Alberta; however, expansion has been limited by the climatic difficulties at harvest, the high labor requirement and the relatively high production cost. If onion production in Alberta is to expand to its potential, information must be developed which will allow the area to become more competitive through increased yield, lower labor requirements, lower production costs, and extended marketing periods. This realization has stimulated work on genetical and environmental factors and on methods of storing and processing the crop.

Dehydration is the most important method for processing of onion. Dehydrated onion enjoys a ready market, can be stored and transported at relatively low cost and, if processed in Alberta, it could easily be marketed through existing domestic and international distribution and retailing channels. This study was undertaken to develop infirmation on the dehydration process of Alberta-grown onions and to relate the volatile losses which occur during processing to the removal of moisture. Specifically, the aim of the study was to explore the interactions between solid, water and aroma compounds through the evaluation of:

Table 6. Alberta onion area, average yield, production, average price and farm value, 1965-1978 (Statistics Canada, 1978a).

Year	Hectares	Average yield (kg/ha)	Production (tonnes)	Average farm price ($/kg)	Total farm value ($1,000)
1965	162	14,988	2,428	0.09	224
1966	154	12,200	1,979	0.10	196
1967	89	4,135	265	0.13	38
1968	129	6,526	842	0.12	99
1969	73	6,588	474	0.13	60
1970	162	8,736	1,415	0.10	142
1971	93	9,759	908	0.10	92
1972	121	11,246	1,361	0.10	215
1973	121	23,707	2,868	0.19	425
1974	89	12,280	847	0.21	178
1975	20	13,610	272	0.15	40
1976	69	28,741	1,983	0.11	224
1977	49	34,214	1,676	0.18	269
1978	49	N/A	N/A	N/A	N/A

(1) Water sorption properties - essential for the interpretation of drying data and directly useful in the design of drying equipment, chemical stability and packaging of dehydrated products.

(2) Dehydration process - studied in terms of evaporation, diffusion and sorption processes.

(3) Analytical procedure for analyzing onion aroma - essential for routine qualitative determinations of the volatiles of fresh and processed onion

(4) Relative volatilities of aromatic components - essential for the interpretation of aroma retention data.

(5) Aroma retention - studied as a function of drying rate, location of the volatiles in the onion, and some physico-chemical properties of the components.

(6) Intensification of aroma - by addition of aroma precursors to the water used for rehydration of the processed product.

II. DEHYDRATION OF ONION

1. LITERATURE REVIEW

1.1 Dehydration of onion as a commodity

Dehydrated onion has become a standard ingredient in nearly every processed food product in which raw onion can be used. A large part of the dehydrated onion production is used as seasoning in production of catsup, chili sauce and meat casseroles, as well as cold cuts, sausages, mayonnaise, salad dressings, pickles, potato chips, crackers and other snack items. Food service outlets also use dehydrated onion because of its convenience in storage, preparation and use. The quantity of dehydrated onion and other dehydrated horticultural crops sold to the retail market is, however, still very small and this can be attributed, in part, to the large loss of flavour which occurs during processing.

The oldest commercial method of onion dehydration involved the use of tunnel driers, (Van Arsdel and Copley, 1964). Chopped or diced onions were spread evenly on wooden trays, 6.1 kg/m^2, and hot air between 71 and 88°C was blown on the onion in the first stage of drying for three to four hours. Cooler air at 49°C was used at the later stage to remove moisture from the onions. When the onions were dried to between 5 and 7% moisture they were transferred to bins and dried in hot air until the desired moisture level of 3 to 4% was obtained (Van Arsdel and Copley, 1964 ; Noyes, 1969).

Drying on wooden trays was effective and relatively inexpensive except for one major problem. Partially dehydrated onions are highly adhesive and they tend to adhere to the wooden trays. If not properly removed, these adhered particles would char and burn under prolonged

exposure to the constant heat. The only means of removal was by scraping, and washing. Sometimes loses due to mechanical injury and burning reached as high as 10%. Furthermore, wooden trays had a much shorter life span than expected due to scrubbings and washings (Van Arsdel and Copley, 1964; Noyes, 1969).

The introduction of stainless steel conveyor belt dehydrators eliminated most of the damage caused by adhesion. It also provided a means of continuous processing. In a conveyor belt dehydrator the onion slices are automatically spread on a continuous stainless steel perforated belt. Hot air is blown through the bed of onions on the belt, alternately flowing upward in one section of the drier and downward in one or more following sections. The temperature of the air is gradually reduced from about 80°C to about 50°C, as the product moves through the stages of the drier. The product leaves the belt drier at about 6% moisture in approximately 6 h (Stark, 1962).

The partially dried slices are then "finished" in bins, where some additional moisture is removed and inequalities, "wet spots" and "dry spots", are mostly evened out. In this finish drying operation, the product is brought to less than 4% mean moisture content by blowing warm dehumidified air, temperature 49°C and absolute humidity not over 0.003 kg moisture per kg of dry air, through ductwork into the perforated bin bottom and through the product. This operation may take from 12 to 30 h, depending on the size of the dry pieces, the desired final moisture, the volume, temperature, and humidity of the air forced through the product, the initial moisture of material going into the bins, and the depth of material in the bin (Van Arsdel and Copley, 1964; Noyes, 1969).

Conveyor belt dehydrators are however, still wasteful of space, time, manpower and product. To overcome these problems, Van Gelder (1962) developed and patented a process by which space requirements can be reduced. The process is based upon the discovery that the rate of gaseous treatment of materials is enhanced when the material is subjected simultaneously to: a) a high velocity gas flow, passing upwards through the material, sufficient to cause fluidization of the material within the treating zone, and b) a vibratory motion of such a nature and extent that the fresh surfaces of the material are exposed to the flow of the treating gas.

According to this process, treatment (drying, cooling or sterilization) can be with heated, chilled, dehydrated and/or humidified gases, or any combination of these. As a further variation, treatment may be accompanied by exposure of the material to radiation of the high frequency range (e.g., microwaves or radiation in the infrared range), or to ultrasonic sound waves, or to a combination of these.

Fleming & Poole (1969) described a four-stage fluidized bed drying system for onion dehydration which they claimed can produce 500 kg of onions per hour containing 3.5% moisture from a wet basis of 86%. The system, according to the authors, uses standard fan power mixer units in a variety of ways to produce optimum conditions of air circulation for the various stages of drying. It is efficient, has guaranteed uniformity of production and is sanitary.

Rogers Brothers Company of California, one of the four major processors of dehydrated onion (the other three are: Basic Vegetable Products Inc., Vacaville, Ca.; Gentry International, Inc., Gilroy, Ca.;

and Gilroy Foods Inc., Gilroy, Ca.), in 1971, completed the construction of a 1.2 million dollar expansion of their plant in Livingston, California (Anon. 1971). This expansion features a 66 m long dehydrator built by Proctor and Schwartz, Inc. of Philadelphia, Pennsylvania. This four-stage dryer is believed to be the largest onion dehydrator ever built. It has a capacity of over 4,500 kg/h of raw product and incorporates most of the desirable features of the above described driers.

Dehydrated onions are commercially sold in may size classifications; the most common types are sliced, chopped, minced, granulated and powdered (Foster, 1968). As much as one-third of the final dehydrated material may end up as onion powder, although much care is exercised during all the handling to minimize the formation of this relatively lower-valued product.

For institutional and military trade most dehydrated onions are packed in hermetically sealed No. 10 cans; for shipment to remanufacturers using larger quantities, 0.022 m^3 triple-friction top cans and 0.118 to 0.25 m^3 fiberboard drums with polyethylene or aluminum foil moisture barriers were used. A variety of containers, such as plastic or aluminum bags, jars, and chipboard boxes, are used for the growing retail market.

The increased size and efficiency of the onion dehydration plants in recent years, has resulted mainly from improved technology and production methods which have enhanced the performance and quality of the product to such an extent that, at least in California, a stable industry has developed. If further growth of the onion dehydration industry is to be expected, improvement of the product quality through better understanding of the drying process is essential.

1.2 Water Sorption Properties

An important characteristic of food products, which influences several aspects of drying and storage is their equilibrium moisture content. There is a well established relationship between water sorption isotherms and chemical, physical and stability characteristics of dehydrated food products (Loncin *et al.*, 1968; Labuza, 1968; Labuza *et al.*, 1970; Karel, 1975). Sorption isotherms of food products constitute an essential part of the theory of drying (King, 1968) and also provide information directly useful in the design of drying equipment. Knowledge of the equilibrium moisture content is also important in the prediction of equilibrium conditions after mixing products with varied water activities (Salwin & Slawson, 1959) and in the study of packaging of dehydrated vegetables. The equilibrium values yield information concerning the vapor pressure of water within the package and are thus helpful in estimating, from known permeability data, the effectiveness of the packaging membrane in protecting the dried material against moisture uptake. The determination of equilibrium moisture contents for dehydrated foods also provides valuable information on the thermodynamics of water sorption, since from existing theories (Young & Crowell, 1962), thermodynamic functions can be calculated from the sorption isotherms. Thermodynamic functions allow for the theoretical interpretation of experimental results in accordance with the statements of the theory. For instance, the variation in entropy can be related to the order/disorder

concept, which is useful for the interpretation of such processes as dissolution, crystallization and swelling, which usually occur during water sorption by food products (Iglesias *et al.*, 1975a; Karel, 1975).

Procedures for obtaining water vapor isotherms for foods have been described in detail by Taylor (1961), Karel & Nickerson (1964), Labuza *et al.* (1976) and Troller & Christian (1978). Two are more commonly used. The first is one in which the material is placed in vacuum desiccators containing saturated salt solutions or sulphuric acid solutions which give a certain equilibrium relative humidity. The composition of salt solutions for the various humidities necessary for food isotherms have been compiled by O'Brien (1948), Wink & Sears (1950), Richardson & Malthus (1955) and Rockland (1960). The second method, as used by Makower & Meyers (1943) and Taylor (1961), the vapor pressure of water in equilibrium with a food at a given moisture content is measured by a sensitive manometric system. Relatively high precision (± 0.02 a_w) has been claimed for this technique by Sloan & Labuza (1975) and Labuza *et al.* (1976). Unfortunately, instruments capable of measuring wide vapor pressure differences are cumbersome and extremely fragile. Also, absolute uniform temperatures and a high degree of thermometric accuracy are required.

To describe the equilibrium moisture content, temperature and relative humidity relationships of biological materials, at least 77 equations have been proposed or used (van den Berg & Bruin, 1978). These models eventually fall under three types of approaches: a)

kinetic, b) potential, and c) capillary condensation.

The classical kinetic approach to isotherms has been that of Langmuir (1918). This model describes the adsorption of a monolayer of vapour on the surface of the solid material and results in an isotherm consisting of two portions: an initial curved section which is concave downward, and a straight section. The isotherm may be derived from either a balance of the vaporization-condensation rate or from molecular vibration residence times, and it may also be derived thermodynamically. Unfortunately, for most food material, the Langmuir model does not hold for the following reasons: 1) the surface is composed of many differing sites with different attractions for water vapour; 2) interaction between absorbed molecules probably occurs, whereas the model assumes no interaction; and 3) the maximum adsorption possible is much larger than just the monolayer. An improvement upon the Langmuir model was made by Freundlich (1926). He assumed that the isotherm was composed of a series of monolayers adsorbing on a surface composed of heterogeneous sites. In this case, the total amount adsorbed is equal to the sum of the Langmuir isotherms, each with its own heat of adsorption. As is the case for the Langmuir isotherm, this is of little relevance to most food materials (Labuza, 1968).

The isotherm model with the greatest popularity is the Brunauer-Emmett-Teller (B.E.T.) isotherm after the work of Brunauer *et al.* (1938). The basic assumptions made are: 1) the heat of sorption for the first layer is constant and equal to the total heat of vaporization plus a constant heat due to site interaction, 2) the

heat of sorption for all layers above the monolayer is equal to the heat of vaporization, and 3) sorption occurs only on specific sites. Since these assumptions are not entirely true for most materials, the B.E.T. model usually holds only between activities from 0.1 to 0.5, but this is enough to calculate the monolayer coverage of the surface by water.

Several isotherm theories have been based on the force field caused by the surface of the solid material, of which the Polanyi (1928) and the Harkins-Jura (1944) models are most important. The disadvantage of these models is, however, that they cannot successfully be used to predict the monolayer value which is of prime importance to the food field (Labuza, 1968).

Sorption models based on the capillary condensation phenomenon include among others, the Henderson (1952), Kuhn (1964) and Day & Nelson (1965) equations. These and other models have been reviewed by Young & Crowell (1962), Adamson (1967), Labuza (1968), and recently by Chirife & Inglesias (1978), who summarized 23 equations for fitting water sorption isotherms of foods.

Extensive measurements of moisture sorption have been reported for dehydrated potatoes (LeMaguer *et al.*, 1976; Strolle & Cording, 1965; Görling, 1958), wheat flour, starch and gluten (Bushuk & Winkler, 1957), sugar beet root (Iglesias *et al.*, 1975a), corn (Chen & Clayton, 1971), rice (Zuritz *et al.*, 1979), wheat (Day & Nelson, 1965), garlic powder (Pruthi *et al.*, 1959), grapefruit, banana, pineapple, peppermint, laurel, cardamon, thyme, chamomile, anise, nutmeg,

cinnamon, lentil, tapioca, ginger and others (Wolf *et al.*, 1973; Iglesias & Chirife, 1976). Thermodynamic quantities found from the temperature dependence of sorption isotherms have also been reported for several commodities including potato starch (Stitt, 1958), and sugar beet root and its main components (Iglesias *et al.*, 1975a, b), but little published information is available on the water sorption properties of dehydrated onion.

1.3 Dehydration of solid foods

In spite of the considerable effort and some progress made in recent years in the understanding of the chemical and biochemical changes that occur during dehydration and in some isolated studies on the mechanism of food dehydration (Jason, 1958; Fish, 1958; Saravacos & Charm, 1962; Roman *et al.*, 1979), drying of solid foods remains still largely an art (Fulford, 1969).

The drying of solid foods, such as onion, is usually taken to mean the removal of moisture from the solid by evaporation. The evaporated moisture is carried away by means of an external drying medium circulated over the drying solid; often this medium consists of dry air, which may also be heated to act as the heat transfer medium.

The basic theory of the drying of solids was developed through the study of inorganic materials, and certain principles of drying in the chemical industry were adapted to the food industry. In the drying of clays and other industrial materials, two periods of drying were found: the constant-rate period and the falling-rate

period. The moisture content at the transition point (critical moisture content) is characteristic of each material for a given set of drying conditions. The mechanism of drying during the constant-rate period is fairly well understood. The rate of drying per unit surface area depends entirely on parameters external to the solid being dried, such as the velocity, temperature and humidity of the drying air. If the external conditions are constant, then the drying rate in this period is constant.

In the constant-rate period it is also known that if all the heat for evaporation of water is supplied in the drying air (convective drying), the temperature of the solid will equilibrate at or close to the wet-bulb temperature of the air. Hence, the material temperature and rate of drying are both fairly easily calculated for this period (Charm, 1971).

In the falling rate period an additional resistance to moisture transfer arises inside the material being dried, since there is no longer free moisture on the entire surface. In many cases, the internal resistance to moisture transfer becomes limiting, so that the various methods which can be used to intensify drying in the constant rate period become of limited use. In addition, the material temperature will no longer be at the wet bulb temperature even in the case of convective drying, so that it becomes necessary to take into account both temperature and moisture content distributions in the body (Fulford, 1969).

There are many published mathematical models available for estimating simultaneous heat and moisture transfer in dehydrated material (Henry, 1948; Krischer, 1963; Lykov & Mikhailov, 1965; Whitney & Porterfield, 1968; King, 1968; Harmathy, 1969; Berger & Pei, 1973; Hayakawa & Russen, 1977). The main difficulty in describing transport of heat and mass inside porous food materials, based on microscopic analysis, is that the geometry of the structure is not easily described quantitatively, while the individual transport processes relate to local values of temperature, pressure and composition.

The mathematical model provided by Henry (1948) accounts for the interaction which occurs during the simultaneous transfer of moisture and heat. According to this model, moisture transport is assumed to occur only in the vapor phase, and the interaction between heat and mass transfer is accomplished with the assumption that water vapor concentration is at all times during the transfer process a linear function of moisture content and temperature. Capillarity within the air space and hysteresis are neglected. Krischer (1963) provided a model consisting of differential heat and mass transfer equations which accounts for simultaneous transfer of water by capillary forces and by vapor diffusion in series, in parallel, or in more complex series and parallel combinations. This model requires the use of two diffusion coefficients to account for the two mechanisms of moisture transfer. Unfortunately, both these quantities depend on the nature of the material, the nature of the pore structure, the moisture content and temperature. The lack of these coefficients and the complicated calculating procedure are

pointed out by Fulford (1969) as major factors detracting from the use of this model. Another approach to generalizing the problem of internal heat and moisture transfer during drying has been made by Lykov & Mikhailov (1965). This approach is based on the application of the methods of the thermodynamics of irreversible processes to the case of internal heat and moisture transfer during drying. Essentially, the moisture transfer is split into two parts, one due to the moisture transfer driving force, which is specially defined in an attempt to encompass most of the mechanisms of moisture transfer and which is characterized by a moisture diffusivity coefficient, and one due to the temperature gradient, which is characterized by the thermo-gradient coefficient. Lykov & Mikhailov's analysis, however, is not rigorous from the non-equilibrium thermodynamic point of view (Bomben *et al.*, 1973). The solutions they give for the set of differential equations all assume constant transport coefficients, making the solutions unsuitable for description of drying foods. Whitney & Porterfield (1968) modified Henry's mathematical model to account for internal heat generation to simulate heating of peanuts.

King (1968) provides an interesting theoretical analysis of simultaneous heat and mass transfer in dehydrated foods which is then successfully used to account for seemingly anomalous observations by various workers related to various moisture diffusivity values. The author, through the combined use of Fick's First Law for binary gaseous diffusion, Fourier's Law of heat conduction in solid, and a modified form of the Clausius-Clapeyron Equation, derives a variable diffusivity equation wherein the effective

diffusivity is a function of both temperature and moisture content. The assumptions made are vapor-phase diffusion only, vapor-sorbed moisture equilibrium at each point within the body, constant sorption heat, and negligible sensible heat.

Harmathy (1969) developed a theory for heat and mass transport based on the assumption that all movement of moisture in porous material takes place in the gaseous phase. This theory seems a good approximation to drying of materials with low initial moisture content. At higher moisture contents, however, capillary transport and/or surface diffusion will take place in addition to the transport of water in the gas phase (King, 1968). The mathematical model comprises a set of second order, nonlinear partial differential equations and was solved numerically with convective boundary conditions.

Berger & Pei (1973) used a mathematical model similar to Krischer's to describe drying of capillary-porous solids. Their model differs in that they use the sorption isotherm in the hygroscopic region and the Clausius-Clapeyron Equation at greater than maximum sorptional moisture content.

Hayakawa & Russen (1977) examined a procedure for estimating simultaneous heat and moisture transfer in an infinite slab of a capillary-porous material when the values of the heat transfer Fourier number were large. For this examination, they used analytical formulae obtained from the Lykov & Mikhailov model and found that the transfer potentials could not be estimated accurately.

In summary, despite efforts made to understand and model the drying process of solid foods, no systematic studies of the dehydration of onions have been reported. It is, therefore, the purpose of this work to present the results of a study aimed at understanding the dehydration of onion slices in terms of sorption and diffusion processes. Rehydration rates at 25 and 40°C are also presented and an attempt to relate the mechanism controlling rehydration to the one controlling moisture removal is made.

2. WATER SORPTION PROPERTIES

2.1 Experimental

Dehydrated chopped onions with an approximately uniform terminal moisture content of 5.2% and pieces 1.5 x 2.5 x 6.5 mm were used. The onion, Yellow Globe, cv. Improved Autumn Spice, was grown at the Alberta Horticultural Research Center, Brooks, Alberta, and air dehydrated in a 0.3 m^2 bed area Vibro Fluidizer (Niro Atomizer, Copenhagen). Drying was carried out in two stages: hot air at 90°C for 1 h, followed by air at 41°C for 15 h. The volume of air used was approximately 500 m^3/h. The moisture content of the dehydrated onions was measured by drying the samples for 48 h at 55°C and under 48.8 mm Hg vacuum.

The adsorption isotherms were determined by placing previously vacuum oven-dried chopped onions in vacuum desiccators containing saturated salt solutions which give different constant relative humidities (Rockland, 1960). The desiccators were kept at constant temperature until equilibrium was reached. The time required for the samples to reach equilibrium varied with the relative humidity and the temperature. Plotting the moisture content of the samples, expressed in kg of water per kg dry solids, versus water activity, a_w, the adsorption isotherms were obtained. To obtain desorption isotherms, the samples equilibrated at 100% relative humidity until they reached constant weight were transferred to atmospheres of lower relative humidities and kept there until equilibrium was reached. The moisture content of the samples, expressed again as kg water per kg dry solids, was plotted versus water activity.

2.2 Results and Discussion

The sorption isotherms at 10, 30 and 45°C of dehydrated Yellow Globe onion are shown in Figure 1 and Figure 2. At low and intermediate water activity, temperature had the normal effect predicted by the theory of physical adsorption, i.e., the quantity of adsorbed water at a given relative humidity increased as the temperature was decreased. At high relative humidity an opposite effect of temperature was observed. This is due to the dominant effect of dissolution of sugars (Salwin & Slawson, 1959; Loncin *et al.*, 1968; Audu *et al.*, 1978), which constitute about 80% of the dry matter (Table 7). For the three temperatures, the isotherms of dehydrated onion are essentially sigmoid in shape and show considerable hysteresis between the adsorption and the desorption branches. This persists over almost the entire water activity range investigated.

The hysteresis is more pronounced at low temperature and lower water activity. The presence of the hysteresis loop means that there are two values of the water activity for any given value of the amount adsorbed. The water activity corresponding to a given sorption is lower along the desorption than the adsorption branch and it follows, on general thermodynamic grounds that, if changes in the solids are ignored, the chemical potential of the adsorbate is lower and accordingly the desorption branch is more likely to correspond to a condition of true equilibrium (Gregg & Sing, 1967).

Several theories have been proposed to explain hysteresis but they are all based on water condensing in the capillaries, which

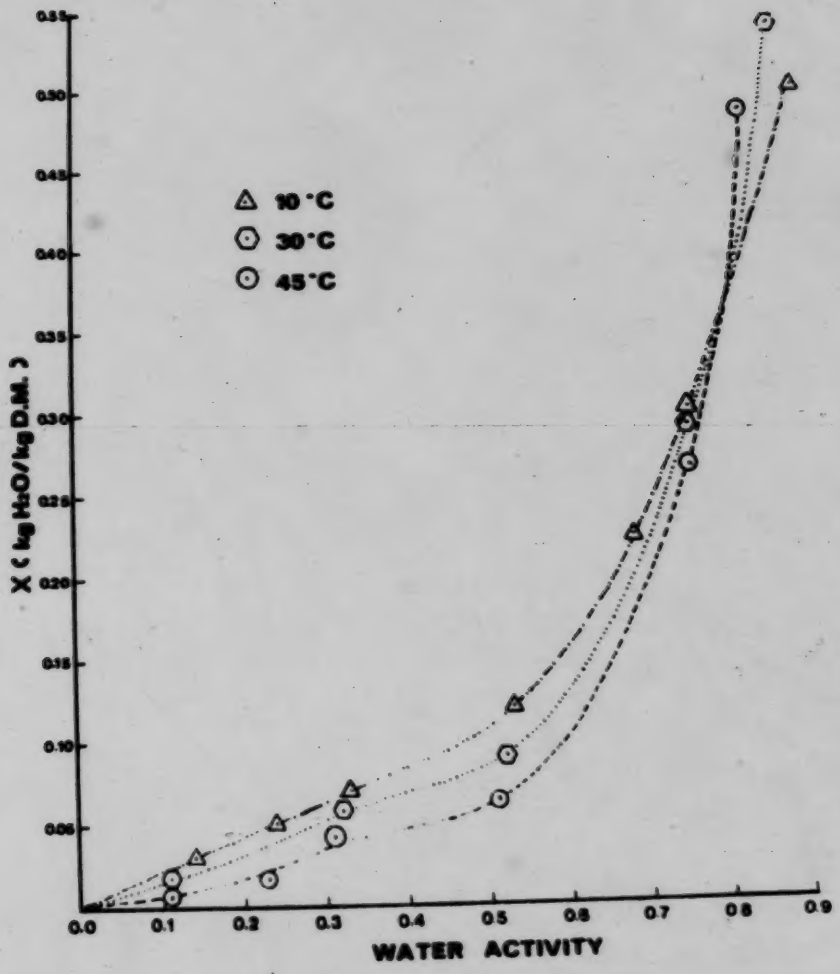


Figure 1. Adsorption isotherms of dehydrated onion at different temperatures.

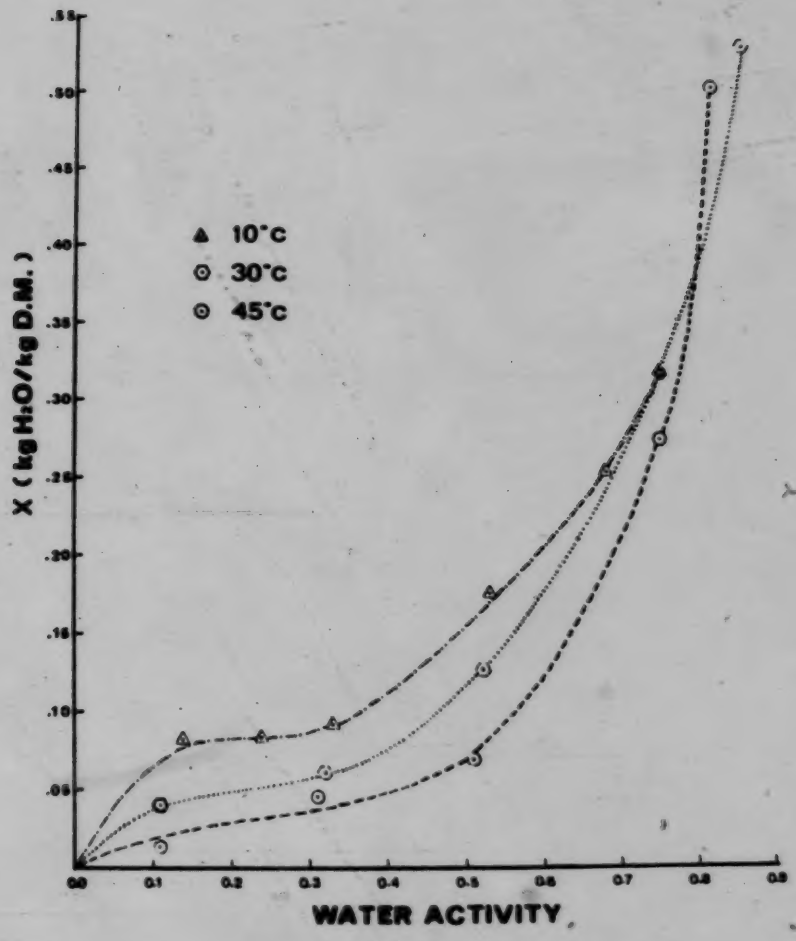


Figure 2. Desorption isotherms of dehydrated onion at different temperatures.

Table 7. Composition of raw and dehydrated onion (Watt & Merrill, 1963)

Component		Raw	Dehydrated
Water	(%)	89.1	4.0
Protein	(g/100 g)	1.5	8.7
Fat	(g/100 g)	0.1	1.3
Carbohydrate	(g/100 g)	8.7	82.1
Calcium	(mg/100 g)	27.0	166.0
Phosphorous	(mg/100 g)	36.0	273.0
Iron	(mg/100 g)	0.5	2.9
Sodium	(mg/100 g)	10.0	88.0
Potassium	(mg/100 g)	157.0	1,383.0
Vitamin A	(I.U.)	40.0	200.0
Thiamine	(mg/100 g)	0.03	0.25
Riboflavin	(mg/100 g)	0.04	0.18
Niacin	(mg/100 g)	0.20	1.4
Ascorbic acid	(mg/100 g)	10.0	35.0

means that hysteresis should occur only at water activity greater than 0.50 - 0.60 (Labuza, 1968). Since this is not the case for the isotherms shown in Figures 1 and 2, it is believed that this type of loop is due to phase transformation of the sugars (Loncin *et al.*, 1968; Iglesias *et al.*, 1975a; Karel, 1975), occuring during moisture adsorption and desorption. The sugars in dehydrated onion are very likely in a very hygroscopic state and an increase in moisture content above that to which they were dried results in their crystallization. The extent to which crystallization proceeds is dependent on the product moisture content, and, during equilibrium moisture content determinations, is dependent on the equilibrium water activity.

Therefore, the shape of the sorption isotherms for dehydrated onions may be directly dependent on the state of the sugars. It has been reported (Karel, 1975) that sucrose may be present in one of several states: crystalline solid, amorphous solid (bound to other food components) and aqueous solution. When onion is dried rapidly, the sugars probably go into the amorphous form. In this form they are very hygroscopic and unstable. However, the very high viscosity of the medium and the presence of the nonsugar fraction of the onion act as support and prevent molecular rearrangement. The sorption of water imparts mobility to the sugar molecules and this mobility results in the transformation of sugar from the metastable amorphous state to the more stable crystalline state. In this process the sugars such as sucrose, glucose and fructose lose water (Iglesias *et al.*, 1975b; Varshney & Ojha, 1975). The sorption

characteristics of amorphous sucrose have been studied by Iglesias *et al.* (1975b) and those of crystalline sucrose, glucose, fructose and lactose by Loncin *et al.* (1968) and Audu *et al.* (1978). Iglesias *et al.* (1975b), have also showed that up to a water activity of 0.375 for 35°C and a water activity of 0.245 for 47°C no crystallization of amorphous sucrose occurs.

From the knowledge of the amorphous and crystalline sucrose isotherms and from the percentages of sugar and nonsugar fractions of the onion (about 80% sugars and 20% nonsugar on a dry basis) the composite sorption isotherm at 30°C was predicted. The results are shown in Figure 3 and compared with the experimental isotherm , the amorphous and crystalline sucrose isotherms (Iglesias *et al.*, 1975b; Loncin *et al.*, 1968), and with the non-sugar fraction isotherm . The predicted isotherm was obtained from the product of the amount of water adsorbed by amorphous sucrose at a given water activity and the percentage of sugars and nonsugars in onion. An examination of the results presented in Figure 3 (Appendix 3) shows that the experimental isotherms, above a water activity of about 0.24, is below the predicted one. This implies that at 30°C the onion sugars are most likely in the amorphous state and that crystallization takes place at intermediate water activities. The same sequence of phenomena takes place at 10°C. At 45°C, however, the experimental points obtained at a_w = 0.11 and a_w = o.24 (Appendix 1) indicate that at these water activities the sugars are probably in the crystalline state; hence, the comparison of the results at 45°C with

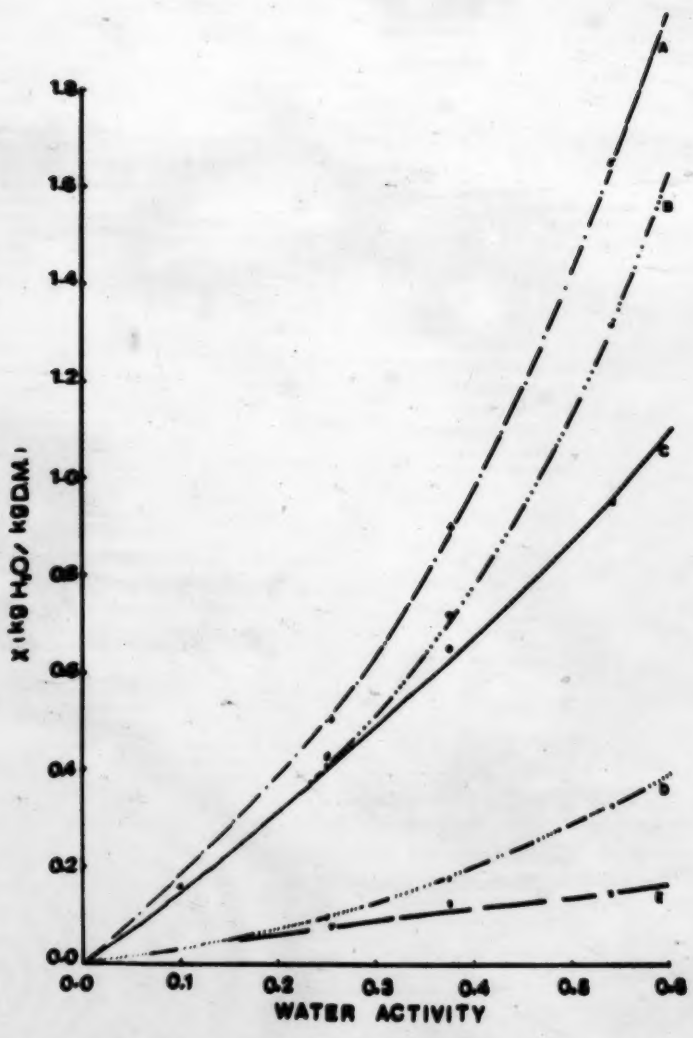


Figure 3. Water vapour adsorption isotherms of dehydrated onion at 30°C; A, amorphous sugar (Inglesias *et al.* 1975b); B, predicted; C, experimental; D, nonsugar fraction of onion; E, crystalline sucrose (Loncin *et al.*, 1968).

those at 30 and 10°C should be made with the understanding that the state of sugars may be different.

The isotherms obtained may be considered a Type II isotherms according to the B.E.T. classification (Gregg & Sing, 1967). The general features of such an isotherm have been discussed extensively by a number of authors including Young & Crowell (1962), Gregg & Sing (1967) and Adamson (1967).

To obtain the relevant values of the monolayer capacity and the heat of sorption, the B.E.T. equation is put in the form of equation (2.1).

$$\frac{a_w}{(1-a_w)X} = \frac{1}{X_m C} + \frac{C-1}{X_m C} a_w \qquad (2.1)$$

where:

$a_w = P_w/P_o$ = water activity = $\frac{\%\ \text{relative humidity}}{100}$

C = constant = $k \exp(\Delta H_{BET}/RT)$

X = equilibrium moisture content, kg adsorbed/kg solid

X_m = monolayer moisture content (same units as X)

A plot of the left hand side of this equation versus water activity gives a straight line in the range of water activity 0.10 - 0.40. From the slope, S, and intercept, I, of this line, X_m and C were calculated. In addition, by assuming the area of a water molecule to be 10.6 Å^2 (Labuza, 1968), the surface area exposed to water, A, was determined from the equation

$$A = X_m \frac{1}{M_{H_2O}} \cdot N \cdot A_{H_2O} = 3.5 \times 10^6 X_m \qquad (2.2)$$

where:

A, X_m = solid surface area, m^2/kg solid; monolayer moisture content, kg H_2O/kg solid

M_{H_2O} = molecular wt. of H_2O = 18 kg/kmole

N = Avagadro's number 6.023×10^{26} molecules/kmole

A_{H_2O} = area of water molecule = 10.6×10^{-20} m^2

Table 8 shows the results from the B.E.T. analysis for adsorption data of dehydrated Yellow Globe onion. It should be noted that for this analysis the values were taken from the smoothed lines, though the sorption isotherms, Figures 1 and 2, show the actual experimental values.

It can be seen that all the B.E.T. values decrease with increasing temperature. This effect has been reported for other food materials by a number of workers, including Iglesias & Chirife (1976) who also stated that the decrease in the B.E.T. monolayer with increasing temperature may be due to a reduction in the total number of active sites for water binding as a result of physical and/or chemical changes induced by temperature. Also, as indicated previously, the change in surface area at 45°C, as determined by the B.E.T. theory, reflects the different state of the sugars in the nonsugar matrix, and from the assumption that crystalline sucrose is present, one would expect much lower surface values. The surface area value calculated from Loncin *et al.*, (1968) data for crystalline sucrose was approximately 100 m^2/g. It should be noted that the value of the constant C is low, and because of this, as pointed out by Gregg & Sing (1967), results

presented in Table 8 should be considered as estimates only.

In Figure 4, a graph of the isosteric heats of sorption as a function of the amount of water vapor adsorbed and desorbed by the onion is presented. The horizontal line indicates the heat of vaporization of water at 30°C. The isosteric heat was calculated graphically from the slopes of the isosteres (P_w vs. T at constant X) using the Clausius-Clapeyron equation in the form

$$\left(\frac{d\ln aw}{d(1/T)}\right)_X = \frac{q_{st}}{R} \qquad (2.3)$$

where R equals 0.46188 kJ/kg K and q_{st} is the isosteric heat of sorption, a differential quantity which varies with the degree of surface coverage, hence with the amount of water adsorbed by the solid (Young & Crowell, 1962). From an examination of Figure 4, it would appear that at low moisture content the heats of desorption are much higher than the adsorption ones. As water is sorbed, the difference decreases and both ad-desorption heats approach the heat of condensation of water at about 30-35 kg H_2O/100 kg DM, which corresponds to about 5 monolayers. At very low moisture content the heats of ad-desorption are nearly one and one-half and twice the heat of vaporization of pure water. This may result from the swelling of the adsorbent, from chemisorption on polar groups, or from a combination of these two phenomena. The swelling process is highly endothermic and may use as much as 50% of the heat produced by the adsorption process, hence, this may account for the low heats of adsorption. The high heat of desorption, on the other

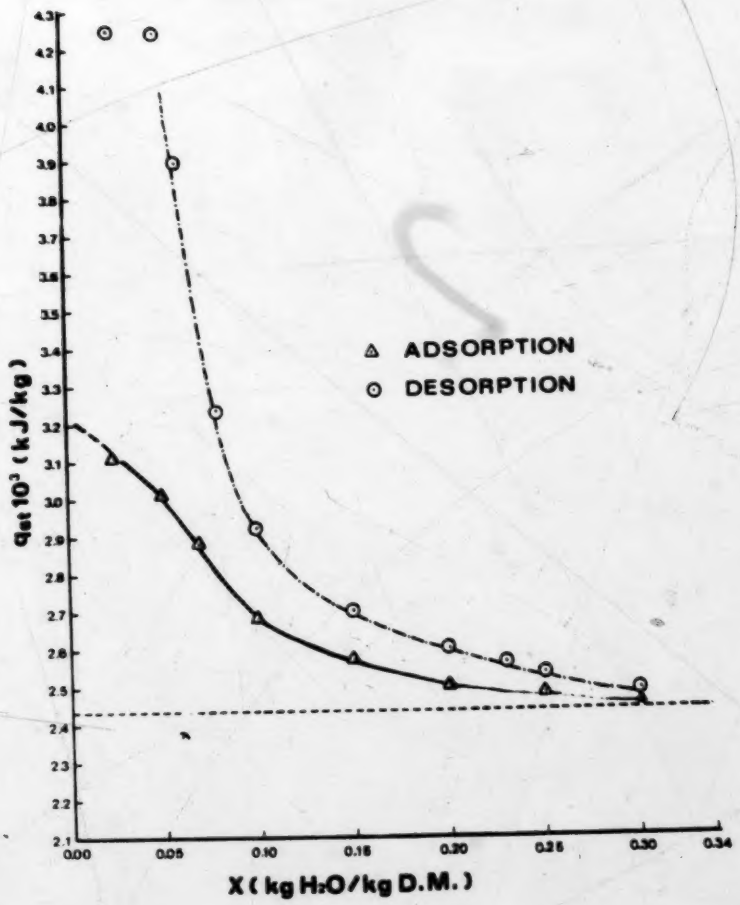


Figure 4. Isosteric heat as a function of amount of water sorbed at 30°C.

hand, may be due to high energy sites resulting from hydrogen-bonds induced in the onion during desorption. These strained hydrogen bonds may be broken with a net evolution of heat, in addition to the heat evolved from the formation of a stable hydrogen bond between the sorbent and the vapour.

A comparison between the isosteric heats presented in Figure 4 and the B.E.T. heats shown in Table 8 indicates that, at the monolayer level, the B.E.T. heats are lower than the isosteric heats. This is in agreement with results reported in the literature (Inglesias & Chirife, 1976).

Table 8. B.E.T. values for sorption data of dehydrated onion.

Temperature °C	Xm kg/100 kg (dry basis)	C	A (m^2/g)	ΔH BET (kJ/kg)	ΔH BET + λ (kJ/kg)
Adsorption					
10	6.67	3.95	233	180	2,657
30	6.20	3.28	217	164	2,597
45	4.71	2.89	164	140	2,535

Another parameter calculated from the isotherms presented in Figure 1 and Figure 2 is the equilibrium heat of sorption, ΔH. This quantity is analogous to the heat of vaporization of a pure substance. But, while the heat of vaporization is a reversible quantity at constant pressure, the equilibrium heat of sorption, by analogy, refers to constant pressure, P, and constant spreading pressure, Φ, as obtained from the Gibbs equation.

The equations for the calculation of ΔH can be derived from thermodynamic considerations as outlined by Hill (1950) and Everett (1950), and as reviewed by Young & Crowell (1962).

For the purpose of this work, ΔH was calculated using the equation

$$\Delta H = RT^2 \left(\frac{d\ \ln P}{dT}\right)_{\Phi} = -R \left(\frac{d\ \ln P}{d(1/T)}\right)_{\Phi} = T\ (S_G - S_s) \qquad (2.4)$$

where S_s = molar entropy of the adsorbed layer and

S_G = entropy of water vapour at T.

From equation (2.4) the molar entropy of the adsorbed layer, which is a measure of the mobility of the adsorbed water molecules, was also calculated. To obtain both ΔH and S_s from equation (4), Φ must first be calculated by integration of the equation

$$\Phi = RT \int_0^P \Gamma\ d(\ln P) \quad (T \text{ const}) = RT \int_0^P \frac{\Gamma}{P}\ dP \qquad (2.5)$$

where, $\Gamma = X/A$, kg H_2O adsorbed/m^2 of solid surface.

For the calculation of Γ the average surface area found from the B.E.T. analysis was used. The integral shown in equation (2.5) was evaluated by carefully plotting Γ/P vs. P and summing the area under the curve.

Figure 5 shows the values of the spreading pressure for adsorption and desorption of water vapour by dehydrated onions at 30°C. Similar plots were obtained for 10 and 45°C.

ΔH and ΔS, where $\Delta S = S_s - S_L$ and S_L is the molar entropy of liquid water at T, were calculated from the slope of the lines obtained by plotting $\ln P$ vs. T at constant Φ and then equation

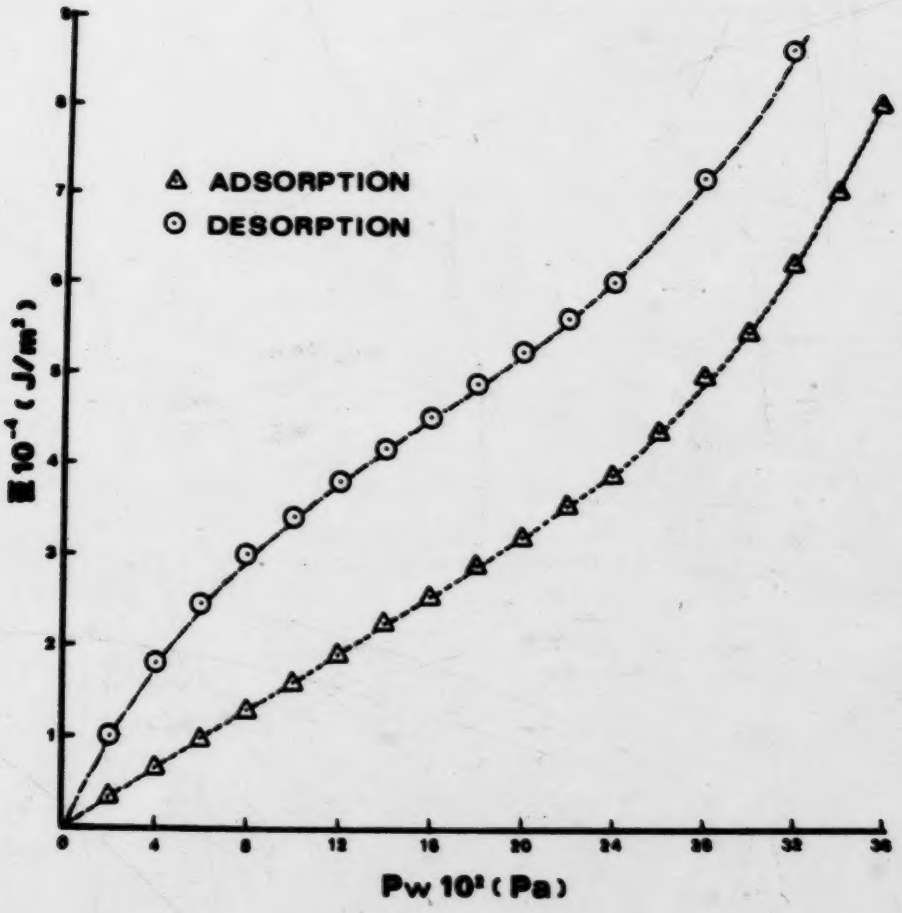


Figure 5. Variation of spreading pressure as a function of water vapor pressure exerted by the onion at 30°C.

(2.4). Figure 6 shows the molar entropy change plotted as a function of amount of water sorbed at 10, 30 and 45°C for the adsorption and desorption processes. It can be seen that at any given moisture content the absolute values of ΔS at 45°C are higher than at 30°C, and the absolute values at 30°C are higher than at 10°C. Also, the ΔS curves for the desorption show a first section where the integral molar entropy increases as the moisture content increases. This section corresponds to water activity below 0.4 and reflects a solid surface which is not completely covered by water molecules; hence no lateral interaction between water molecules occur. Therefore, as compared to a completely covered surface with one monolayer, a molecule of water has more freedom to move towards the low water end. This would result in the maximum absolute value of the entropy to occur at the monolayer, which it does. Following the initial increase, the entropy function decreases up to a moisture content of about 0.25 kg H_2O/kg DM and then remains practically constant. The decrease in entropy after the monolayer is formed means that the state of organization of the water decreases. That is, mobility increases because the second layer of water is interacting with some solute (if in solution) and itself rather than with the surface. At the higher values of X it is observed that ΔS tends towards zero (state of free water), but the effect of sugars is apparent here, with strong deviation at higher temperatures. This is because the presence of solutes tends to organize the water (i.e., increase absolute value of entropy) and, since sugars are more soluble at higher temperature, the amount of solution will be greater, hence

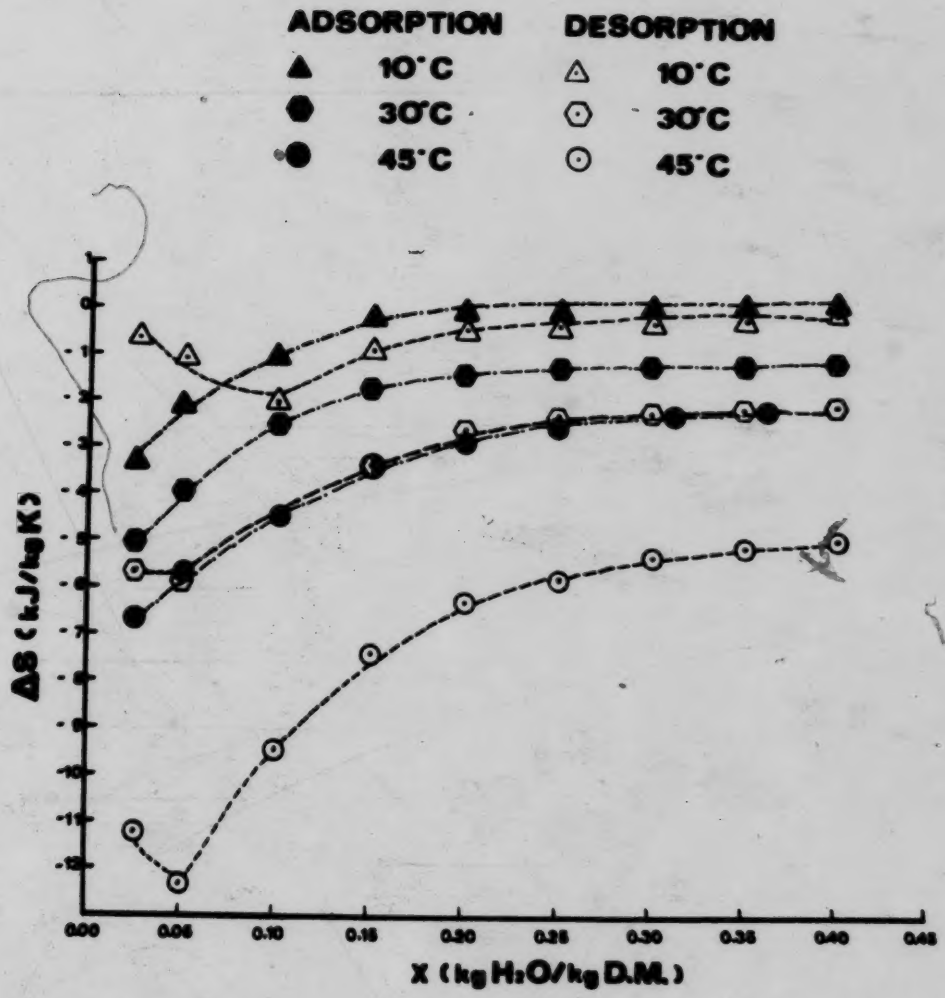


Figure 6. Variation of molar entropy with moisture content.

the entropy higher. A comparison between the ΔS curves for the desorption and those for adsorption show that at the same temperature the ΔS curves for the desorption are always considerably lower that the adsorption ones. This behavior, although expected because of the water being more tightly bound on the desorption branch of the isotherm than on the adsorption one, also suggests that the 'final arrangement' of the water molecules on the surface of the solid may be different depending on whether equilibrium is reached from the 'dry state' (adsorption) or from the 'wet state' (desorption). Also, during the desorption process some of the amorphous sugars undergo crystallization and a concentrated solution appears along with pure sugar, and, therefore, the state of organization of water is a combination of solution effect and desorption effect resulting in greater entropy.

Figure 7 shows the equilibrium heat of sorption as a function of moisture content calculated from the desorption and desorption isotherms at 10, 30 and 45°C. In the case of desorption, ΔH decreases gradually with the increase of sorbed water, and at given X decreases with temperature. With respect to desorption, the equilibrium heat of sorption increases up to the monolayer then decreases, and the three curves are always above the ones obtained for adsorption.

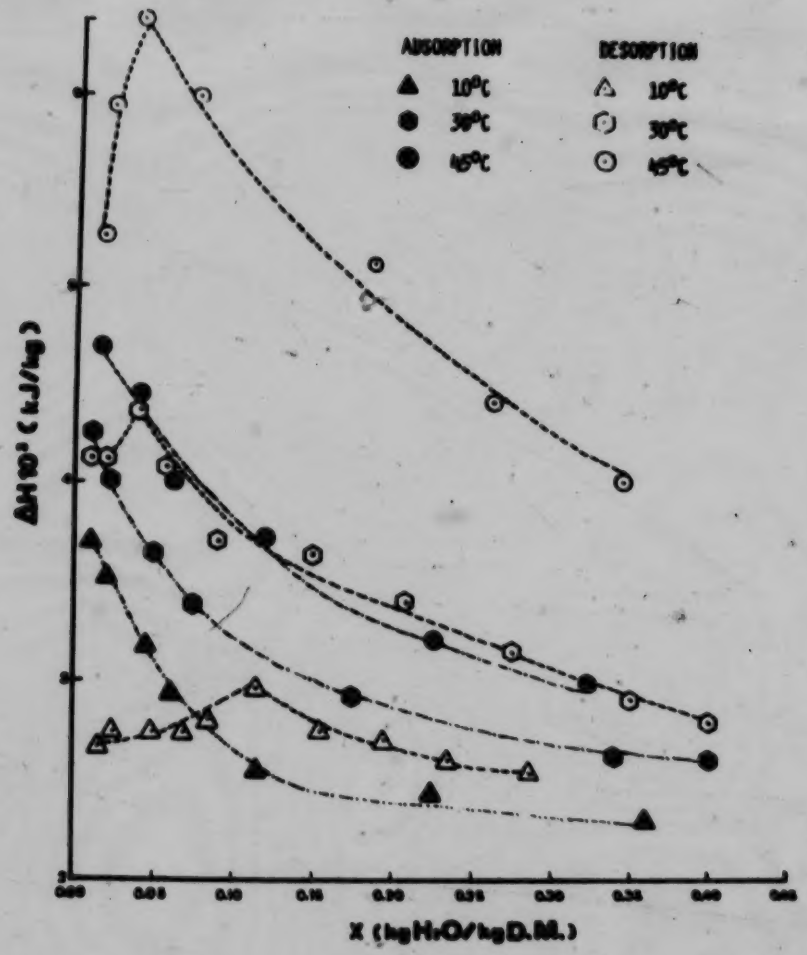


Figure 7. Equilibrium heat of sorption of dehydrated onion as a function of moisture content.

3. DEHYDRATION-REHYDRATION OF ONION

3.1 Experimental

3.1.1 Raw Material

Yellow Globe type onions (cv. Improved Autumn Spice) grown to maturity in experimental plots at the Alberta Horticultural Research Center, Brooks, Alberta were used. The onions were planted in early April, harvested in the middle of September when the tops were down, and cured and graded indoors before storage in bins at 1-2°C. The onions were held in storage for about 1 week before the dehydration experiments were initiated. At this stage, the mean dry matter content of the fresh onion, as estimated by the loss in weight of 10-15 g samples on drying in a vacuum oven at 70°C and 48.8 mm Hg for 6 h, was 12.8%.

3.1.2 Pilot plant scale dehydration

Medium sized bulbs (4.5 - 7.5 cm in diameter) were peeled, sliced (1.5 mm thick) and dehydrated in a 0.3125 m^2 bed area Vibro Fluidizer (Niro Atomizer, Copenhagen). Three temperatures (40, 50 and 65°C) and three air flow rates (5.5, 8.1 and 10.3 m^3/min) were used. The dryer consisted of a perforated plate built into a long, narrow, enclosed chamber. The unit was equipped with an air filter, an air supply fan of the centrifugal type, with built-in damper, an electric air heater, a vibrator, a cyclone, an exhaust fan, also of the centrifugal type with built-in damper, and connecting ducts and control panel. The air velocity was measured using a pitot tube connected to Mark 5 Testing Set (Airflow Developments Ltd., High Wycombe, England), and it was changed by adjusting the damper in the air supply and exhaust fans. The dry-bulb and wet-bulb temperatures (T_{DB} and T_{WB}) were

measured with thermocouples connected to a Honeywell Electronik 16 temperature recorder (Honeywell Ltd., Scarborough, Ontario). The wet-bulb temperature was obtained by covering the end of a thermocouple with a wick immersed in a bottle containing distilled water.

3.1.3 Dehydration rate

Drying curves (X vs. time) were obtained by graphical integration of the thermograms and/or by periodic weighing of onion samples during dehydration. The equilibrium moisture content (X_e) of the onion, required for the drying calculations, was determined by the saturated-salt-solution method as described previously.

3.1.4 Shrinkage measurement

The shrinkage of the onion slices after various times of drying was determined from specific volume measurements by the displacement of toluene.

3.1.5 Rehydration rate

Rehydration was measured in distilled water at 25 and 40°C. Five grams of dehydrated onion were added to 150 ml of distilled water in a 250 ml beaker, mixed thoroughly, and allowed to rehydrate for various lengths of time. At the end of the rehydration period the onion was filtered off using a No. 4 Whatman filter paper and slight vacuum, and weighed. The extent of rehydration was expressed as kg water per kg dry material.

3.2 Theoretical

3.2.1 Model

Following King (1968), the various rate factors involved in drying processes are shown in Figure 8. It can be seen that heat must be transferred from the heat source to the evaporation zone by way of the piece surface. External heat transfer, from the source to the surface, may occur by any of the three principal heat transfer mechanisms; which are conduction, convection and radiation. Internal heat transfer, from the piece surface to the evaporating zone (within the piece), is generally by conduction, but can occur by radiation, particularly if a penetrating radiation, (e.g., microwave) is used. Water vapor generated at the evaporation zone must first travel to the piece surface by any of a variety of internal mass transfer mechanisms (e.g., vapor diffusion, surface diffusion, liquid diffusion, capillary). Then water vapor must travel from the piece surface to the outside environment by external mass transfer processes such as convective mass transfer or diffusion.

For the various mechanisms operating in parallel, such as the three different mechanisms of external heat transfer, the rate-governing mechanism will be that which affords the fastest rate of transfer. On the other hand, for the mechanisms in series, that is, external heat transfer, internal heat transfer, internal mass transfer and external mass transfer, the step with the greatest effect on the rate will be the one which is inherently the slowest, or which requires the largest concentration-difference or temperature-difference driving force. Thus the rate-determining

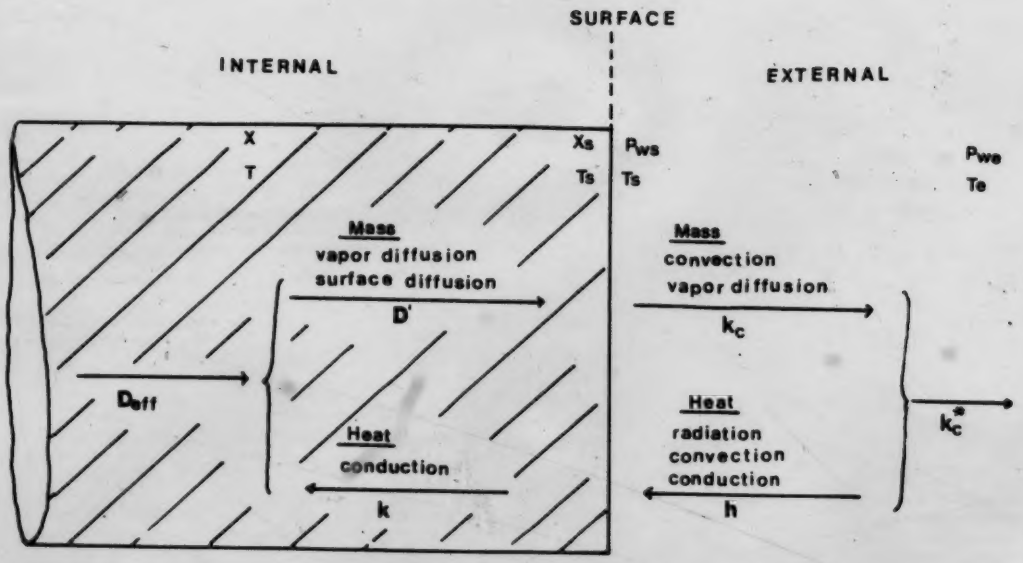


Figure 8. Interaction of heat and mass transfer during drying as proposed by King (1968).

step will be that mechanism which is inherently the slowest out of the assembly of fastest mechanisms for each step.

3.2.2 Equations related to model

From the diffusion model of the form

$$\frac{\partial X}{\partial \theta} = \frac{\partial}{\partial z} \left(D_{eff} \frac{\partial X}{\partial z} \right) \tag{3.1}$$

$$k_c^* \ (X_e - X_s) = - D_{eff} \left(\frac{\partial X}{\partial z} \right)_s \tag{3.2}$$

$$\text{at } \theta = 0 \quad X = X_o$$

where k_c^* and D_{eff} are parameters related to heat and mass transfer coefficients in the external phase and heat and mass transfer coefficients in the internal phase respectively. Through equation (3.3) h, k_c and k_c^* can be calculated

$$N_w = - \frac{dX}{d\theta} \cdot L \frac{\rho_s}{M_w} \left(\frac{V}{V_o} \right)_e = \frac{h}{\Delta H_s} \cdot (T_s - T_e)$$

$$= \frac{k_c}{R_v T} \cdot (P_{we} - P_{ws}) = k_c^* \cdot (X_e - X_s) \cdot \frac{\rho_s}{M_w} \tag{3.3}$$

where N_w = molar mass flux expressed in kmole/m^2s; $dX/d\theta$ = kg H_2O/kg D.M.s; L = one half of the thickness of the onion slice in m; ρ_s = density of the moisture-free solid in kg/m^3; M_w = molecular weight of water = 18 kg/kmole; h = heat transfer coefficient in J/sm^2K; ΔH_s = heat of vaporization of water at the surface temperature (T_s) expressed in J/kmole; k_c = external mass transfer coefficient in m^2/s; R_v = gas constant = 8.314 J/kmole K or Pa m^2/kmole K; P_{we} and P_{ws} = partial pressure of water, at the dry bulb temperature of the air (T_e) and at T_s, respectively,

expressed in Pa; X_e and X_s = moisture content in equilibrium with P_{we} and T_e and with P_{ws} and T_s, respectively; $(V/V_o)_e$ = final over initial volume of onion piece (Figure 13) and k_c^* = combined external mass and heat transfer coefficient.

The combined external heat and mass transfer coefficient is related to k_c and h by the following equation (King, 1968)

$$k_c^* = \frac{M_w}{\rho_s} \cdot \left(\frac{\partial a_w}{\partial X}\right)_T \cdot \frac{P_w^o}{R_v T} \cdot \left(\frac{\beta}{1+\beta}\right) \cdot k_c \qquad (3.4)$$

where

$$\beta = \frac{h\ R\ R_v T^3}{(\Delta H_s)2\ k_c\ a_w P_w^o} = \text{energy out} \qquad (3.5)$$

a_w = water activity; P_w^o = vapor pressure of water at T, expressed in Pa; and R = gas constant = 8.314 J/kmole K. The role of β is analogous to that of another parameter, defined as

$$\alpha = \frac{k\ R\ R_v T^3}{(\Delta H_s)^2\ D^1 a_w P_w^o} = \text{energy in} \qquad (3.6)$$

which, in turn, is related to rate of change of moisture content within the food by equation (3.7)

$$\frac{\rho_s}{M_w} \cdot \left(\frac{\partial X}{\partial \theta}\right) = \frac{\partial}{\partial z}\left\{\frac{D^1 P_w^o}{R_v T} \cdot \frac{P}{P-P_w} \cdot \left(\frac{\partial a_w}{\partial X}\right)_T \cdot \left(\frac{\alpha}{1+\alpha}\right) \cdot \left(\frac{\partial X}{\partial z}\right)\right\} \qquad (3.7)$$

where k = thermal conductivity in W/m K; and D^1 = effective vapor space diffusion coefficient in m^2/s. Equation (3.7) has the form of equation (3.1) and gives

$$D_{eff} = \frac{M_w D^1 P_w^o}{\rho_s R_v T} \cdot \frac{P}{P - P_w} \cdot \left(\frac{\partial a_w}{dX}\right)_T \left(\frac{\alpha}{1 + \alpha}\right) \qquad (3.8)$$

where the term

$$\frac{M_w P_w^o}{\rho_s R_v T} \left(\frac{\partial a_w}{\partial X}\right)_T = \frac{\rho_v}{\rho_L} \qquad (3.9)$$

which represents the ratio of moisture density in the vapor phase (ρ_v) to the moisture density in the condensed phase (ρ_L).

As pointed out by King (1968), the effective diffusivity given by equation (3.8) can be rationalized through a simple physical concept: equation (3.1) describes the removal of water from a source by means of a moisture gradient driving force. The source (left-hand side of the equation) is a condensed phase, the sorbate, while the transport (right-hand side) occurs through the vapor phase. At any time there is considerably more moisture in the condensed phase than in the vapor phase, hence, as moisture leaves by diffusion out through the vapor it is continuously replaced by evaporation from the condensed phase.

3.2.3 Mathematical solution of equations

Mathematical solution of equations (3.1) and (3.2) is available for constant D_{eff} (Crank, 1975) and therefore by means of the Gurney-Lurie charts (Carslaw & Jaeger, 1959) D_{eff} together with the equivalent Biot number (B_i^*) and Fourier number (F_o) were calculated as shown in Appendix (5). Also, from equation (3.8) and (3.9) the effective vapor space diffusion (D^1) was then calculated

$$D^1 = D_{eff} \cdot \frac{\rho_L}{\rho_v} \cdot \left(\frac{\alpha-1}{\alpha}\right) = C_2 D \qquad (3.10)$$

where C_2 = constant reflecting the geometry of the porous medium and D = binary diffusivity in the free gas, = 0.256 cm^2/s at 25°C for H_2O - air.

3.3 Results and Discussion

3.3.1 Dehydration rate

Figures 9 and 10 show typical experimental results in terms of average moisture content of the onion in the drier as a function of time for three representative drying air temperatures and three drying air velocities. It should be noted that for a very short period, at the beginning of drying, in the drier there existed a bottom 'dry' layer and an upper 'wet' layer. If one neglects this very early phase of drying on the basis that the ratio of mass of dry air (m_{DA}) to the mass of dry matter (m_{DM}) was high and that the bed was vibrated occasionally, if follows that the behavior of the individual slices should follow the behavior of the bed, hence, the results can be interpreted using the above-described model.

From the drying rate curves (Figures 11 and 12), the dry bulb temperature of the drying air (T_e), the surface temperature (T_s) and the heat of vaporization of water at T_s, the heat transfer coefficient was calculated. The values obtained for experiments conducted at three temperatures and three air flow rates are presented in Table 9 together with external mass transfer coefficients (k_c), external heat and mass transfer coefficients (k_c^*) and the parameter β. It can be seen that the heat transfer coefficient increases with the rise in air velocity and remains practically constant with the rise in temperature. This implies that external resistances decreased when air velocity was increased and transfer of water improved.

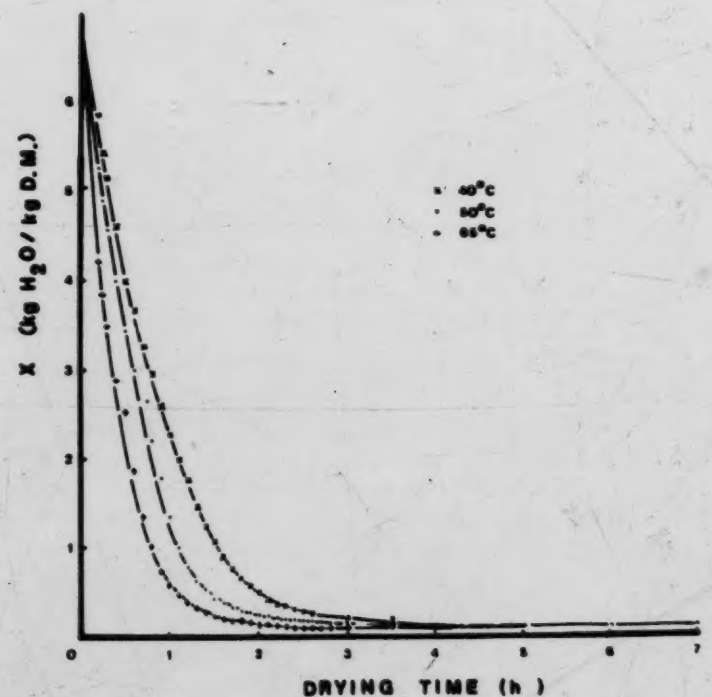


Figure 9. Effect of temperature on the moisture content of onion slices. Drying conditions: Yellow Globe type onion slices 1½ mm thick; air flow rate 8.1 m^3/min.

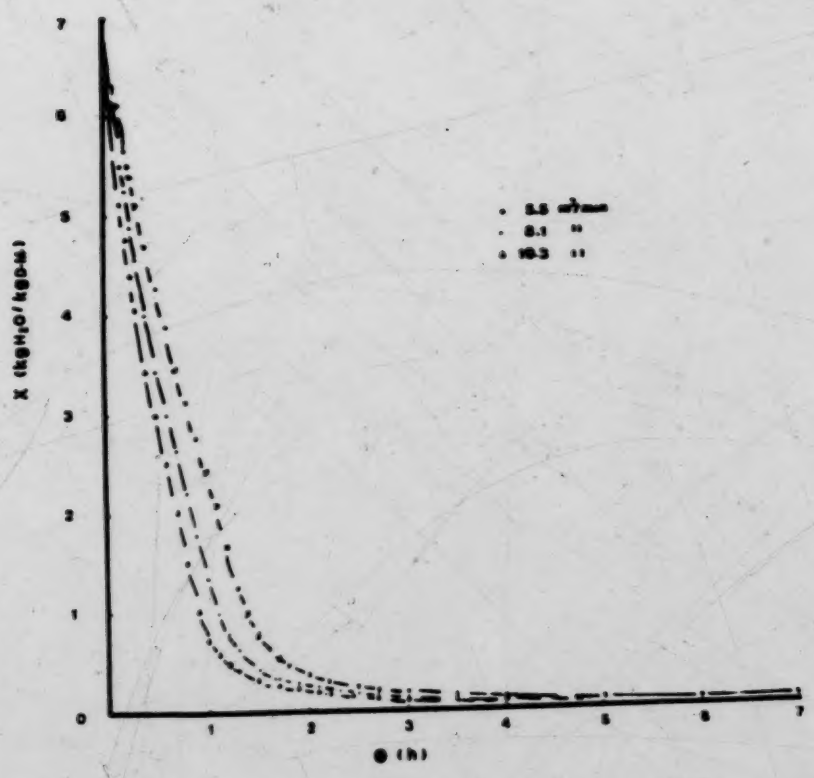


Figure 10. Effect of drying air flow rate on the moisture content of onion slices. Drying conditions: Yellow Globe type onion slices 1½ mm thick, dry bulb temperature of the air, 50°C.

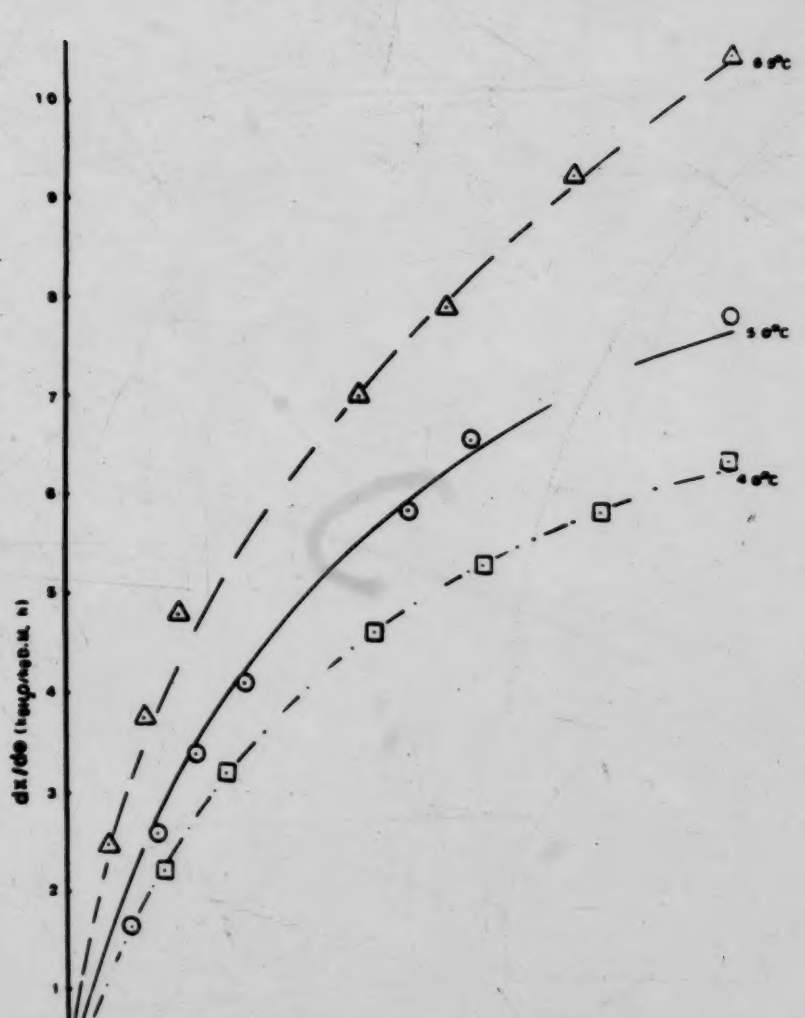


Figure 11. Rate of dehydration of onion slices at 40, 50 and 65°C.

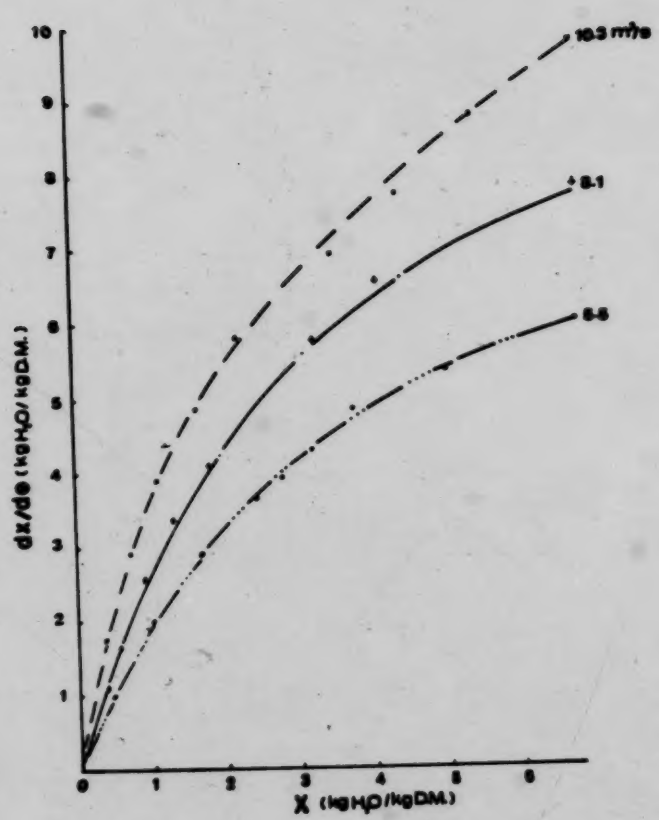


Figure 12. Rate of dehydration of onion slices at 5.5, 8.1 and 10.3 m^3/min air flow rate.

Table 9. Effect of temperature and drying air flow rate on heat (h), mass (k_c), combined external heat and mass (k_c^*) transfer coefficients and parameter β .

Air characteristics							
T_{DB} (^oC)	T_{WB} (^oC)	$\dot{V}$ (m^3/min)	ρ (kg/m^3)	h (J/sm^2K)	k_c (m/s)	k_c^* (m/s)	β
40	18.6	8.1	1.140	42.5	4.38×10^{-2}	3.4×10^{-6}	1.03
50	21.8	8.1	1.151	37.8	3.51×10^{-2}	4.0×10^{-6}	0.96
65	26.5	8.1	1.134	36.1	3.90×10^{-2}	7.0×10^{-6}	0.20
50	20.6	5.5	1.108	28.4	2.53×10^{-2}	3.2×10^{-6}	1.58
50	22.5	10.3	1.099	48.2	4.38×10^{-2}	4.8×10^{-6}	0.97

The values of k_c and k_c^* were calculated using equation (3.3), together with the psychrometric chart, to obtain the water activity, hence, the values of P_{we} and P_{ws} corresponding to T_e and T_s, and the desorption isotherms, to obtain the values of X_e and X_s corresponding to P_{we} and P_{ws}. Although not as clearly as the heat transfer coefficients, they indicate that external resistances were indeed important.

The parameter β, which determines the degree of external mass or heat transfer control, decreases with increasing temperature. This means that at higher temperature the process is more heat transfer controlled. That is, the quantity of energy reaching the surface is what controls the amount of water removed and it is relatively easy to eliminate that water vapor from the surface through the mass transfer mechanism. Also, the fact that β decreases with increasing temperature means that the rise in temperature improved more the heat transfer. Hence, the higher drying rate resulted from improved mass transfer. This is apparent from the values of k_c^* (Table 9), which doubled when the temperature was raised from 40 to 65°C. At constant temperature and variable air velocity, β decreased with the first rise in air velocity but remained unchanged with the second increase. This indicates that with the first rise in air velocity the dehydration rate underwent a transition from external mass transfer control to external heat transfer control. However, once this transition had taken place, further increase in air velocity did not effect the controlling mechanism.

From equation (3.3) one can see that the quantity of energy transmitted to the food can be affected either by the heat transfer coefficient (h) or by the driving force ΔT. By increasing the air velocity, studies (Charm, 1971) have shown that h increases approximately as $v^{0.8}$. A calculation from the values in Table 9 for the different velocities shows the expected relationships. On the other hand, as shown in the same table, an increase in air temperature modifies the total energy transferred without altering significantly the external heat and mass transfer coefficients.

In Table 10 are presented the values of D_{eff}, B_i^*, D^1, C_2, α and τ, calculated as indicated previously for experiments conducted at constant air velocity and variable temperature and constant drying air temperature. Beginning with the parameter α, whose role is entirely analogous to that of β, in determining whether the rate is internally mass transfer- or heat transfer-controlled, it can be seen that α is well above 1. Hence, the internal mechanism was mass transfer controlled, which means that, although enough energy arrived at the evaporating zone (within the piece), the transfer of the water vapor from the evaporating zone to the surface was limited. At constant air velocity and variable temperature α decreased with increasing temperature, which implies that the dependence on mass transfer decreased.

Effective diffusion coefficient (D_{eff}) increased with air velocity and with temperature (Table 10). The increase in D_{eff} with temperature is in agreement with the kinetic theory of gases

Table 10. Effect of drying air temperature and flow rate on effective diffusion coefficient (Deff), Biot number (B_i^*), effective vapor space diffusion (D^1), parameter α and constants reflecting geometry of porous material, C_2 and τ, at X = 4 and X = 0.4 kg H_2O/kg D.M.

Air characteristics		D_{eff} (m^2/s)		B_i^*		(m^2/s)	C_2	α	τ
T_{DB} (°C)	$\dot{v}$ (m^3/min)	X_1	X_2	X_1	X_2	X_1	X_1	X_1	X_1
40	8.1	4.11×10^{-11}	1.72×10^{-11}	62	38	2.62×10^{-6}	0.10	59	1.10
50	8.1	5.36×10^{-11}	2.94×10^{-11}	56	26	2.85×10^{-6}	0.11	42	1.07
65	8.1	9.54×10^{-11}	7.08×10^{-11}	55	25	3.96×10^{-6}	0.15	22	0.92
50	5.5	4.00×10^{-11}	1.50×10^{-11}	60	34	2.27×10^{-6}	0.09	56	1.20
50	10.3	7.35×10^{-11}	3.94×10^{-11}	49	24	3.78×10^{-6}	0.15	32	0.93

[1] *X = 4 kg H_2O/kg D.M.*

[2] *X = 0.4 kg H_2O/kg D.M.*

which predicts a significant increase in diffusivity as temperature increases (Loncin & Merson, 1979). At constant pressure, diffusivity in gas systems varies approximately as $T^{1.75}$ and, as shown in equation (3.8), D_{eff} is proportional to D^1 so that when D^1 increased with temperature, so did D_{eff}. Air velocity should not have had a direct effect on D_{eff}; however, as shown in equation (3.2), D_{eff} is proportional to k_c^* and to $(X_e - X_s)$, so that when k_c^* improved slightly with air velocity, greater driving force $(X_e - X_s)$ resulted and D_{eff} increased.

A comparison between the values of D_{eff} obtained for X = 4.0 and X = 0.4 shows that D_{eff} decreased with the decrease in moisture content. This is consistent with the results reported by other workers (Loncin & Merson, 1979), and indicates that diffusional limits to moisture transport within pieces to the vapor-piece interface become important at the lower moisture content.

Water vapor diffusivity for onion slices has not been reported previously, but it has been determined for other foods, such as fish muscle (Jason, 1958), potatoes (Saravacos & Charm, 1962; Fish, 1958), pepperoni (Palumbo *et al.*, 1977), and apple pieces (Roman *et al.*, 1979). The results for onion slices are comparable to those reported in the literature.

The equivalent Biot number $(k_c^* L/D_{eff})$, which measures the relative external over internal resistance, was found to be large (Table 10). This means that internal resistances were controlling. Temperature had practically no effect on the Biot number,

implying that with the rise in temperature both external (from the values of k_c^*, Table 9) and internal (from the values of D_{eff}, Table 10) resistences were affected to the same degree, and the net effect was virtually zero. With the decrease in moisture content, the B_i^* decreased, meaning that internal mass transfer was probably improved as a result of the temperature rise in the product.

The parameters C_2 and τ, which are related by the expression C_2 = voidage (ξ)/tortuosity (τ^2) varied with temperature and air velocity. In both cases (constant air velocity and constant drying temperature) the maximum compactness seemed to occur at low velocity and low temperature.

3.3.2 Shrinkage measurement

The relationship between the volume as a proportion of the original volume and moisture content of the onion slices dehydrated at 50°C and 8.1 m^3/min air flow rate is shown in Figure 13. It can be seen that as drying progressed, shrinkage increased and at the end of dehydration it was over 89%. At a given moisture content, differences of less than 1% in shrinkage were found between samples dehydrated at different rates. Suzuki *et al.*, (1976) who, using a photographic technique, measured shrinkage of carrot, potato and radish during air-drying, obtained comparable results. The results presented in Figure 13 were calculated from specific gravity measurements (Appendix 6), hence, they reflect the 'average' shrinkage. However, if this shrinkage in volume is assumed to correspond to the volume of water removed

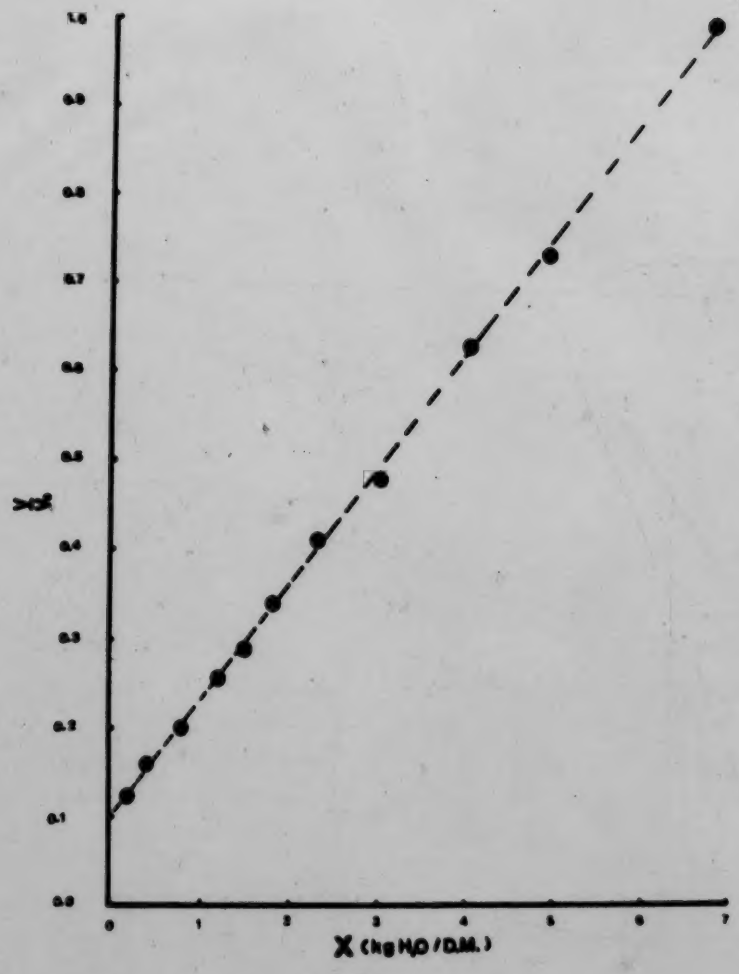


Figure 13. Relationship between volume as a proportion of the original volume, and moisture content of onion slices.

during dehydration, the surface area as a proportion of the initial surface area can be expressed as

$$\frac{A}{A_o} = \left(\frac{V}{V_o}\right)^{2/3} \tag{3.11}$$

The volume of the fresh onion is equal to the sum of the volume of removable water and the volume at equilibrium, so that equation (3.11) can be converted to

$$\frac{A}{A_o} = \left[\frac{V_e + [(w - w_e)/\rho_{H_2O}]}{V_e + [(w_o - w_e)/\rho_{H_2O}]}\right]^{2/3} \tag{3.12}$$

But the density of water, $\rho_{H_2O} = 1.00$ g/cm^3 hence

$$\frac{A}{A_o} = \left[\frac{w + w_e\,(1/\rho_e - 1)}{w_o + w_e\,(1/\rho_e - 1)}\right]^{2/3} \tag{3.13}$$

and if

$$a = X_e(1/\rho_e - 1) + 1/\rho_e \tag{3.14}$$

$$\frac{A}{A_o} = \left(\frac{X + a}{X_o + a}\right)^{2/3} \tag{3.15}$$

The parameter, a, calculated for the experiments conducted at 40, 50 and 65°C, was 0.73, 0.72 and 0.69, respectively. Kilpatrick, *et al.*, (1955) reported a value of a = 0.80 for potatoes dried in a tunnel drier.

3.3.3 Rehydration rate

Rates of rehydration vs. time at 40 and 25°C for onion samples dehydrated with air at 50°C are shown in Figure 14 . It is immediately apparent that at 40°C the rate of rehydration was faster than at 25°C. After approximately 1 h the amount of water

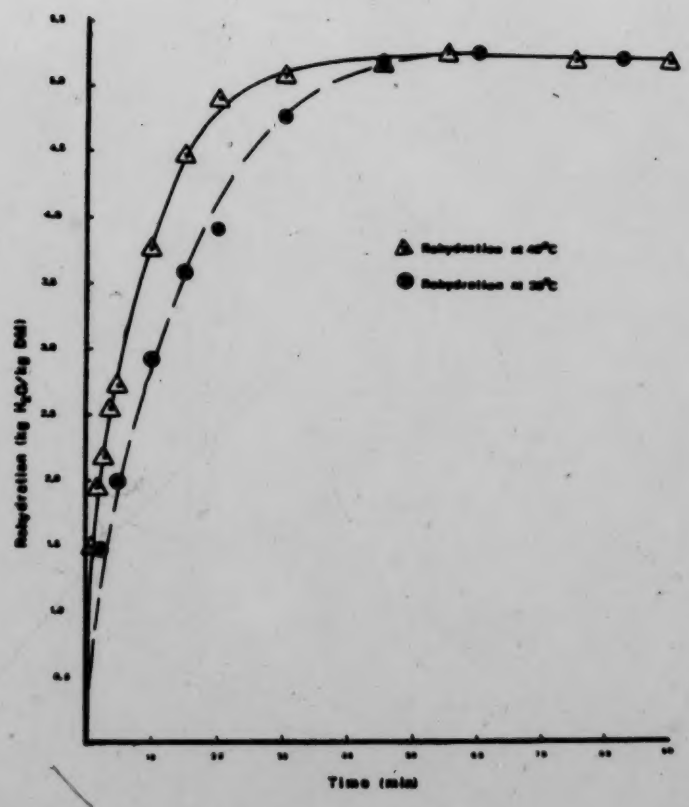


Figure 14. Rehydration of Improved Autumn Spice onion slices dehydrated at 50°C.

absorbed at the two temperatures was about the same and rehydration ceased. No real differences were found, both in rate and final volume of water absorbed, between samples rehydrated at different air temperatures or air flow rates. The present study showed small decreases in rehydration volume and rehydration rate as the dehydration rate increases, but the differences were not significant. These results agree with those reported by Shimazu *et al.*, (1965) for White Globe onion.

When the rehydration data obtained at 25 and 40°C were plotted as log $(X_\infty - X)$ vs. time, straight lines resulted for the region of moisture contents of 6.2×10^{-2} kg H_2O/kg D.M. to about 5.2 kg H_2O/kg D.M. (Figure 15). Ignoring external resistances to heat and mass transfer (i.e., $B_i^* = \infty$), the average liquid diffusivity was calculated through equation (3.16) where $(X - X_e)$ is a function of $D\theta/L^2$.

$$\frac{X - X_e}{X_o - X_e} = \frac{8}{\pi^2} \; e - D\theta \; (\pi/2L)^2 \qquad (3.16)$$

The diffusivity values are also shown in Figure 15.

When the values of diffusivity of water during dehydration and rehydration are compared, it is found that at the same temperature $D_{rehydration}$ is higher than $D_{dehydration}$ (2.33×10^{-10} m^2/s vs. 4.11×10^{-11} m^2/s). This is not surprising since, during rehydration, in addition to liquid diffusion, other mechanisms such as capillary flow, flow caused by gravity and adsorption are operating.

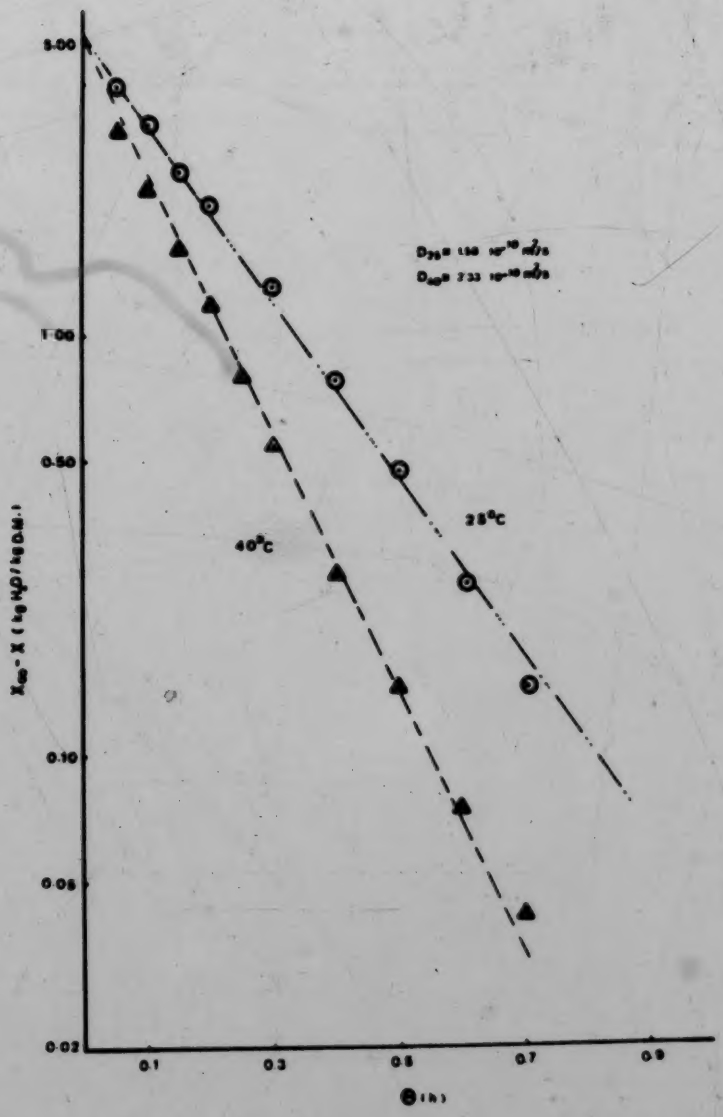


Figure 15. Rehydration of onion slices at 25 and 40°C.

III. AROMA RETENTION DURING DEHYDRATION OF ONION

I. LITERATURE REVIEW

I.1 Chemistry and Analysis

The characteristic aroma or odor of onions is due to volatiles consisting mostly of sulfur compounds. The volatiles are absent in intact tissue. However, when the tissue is sliced, reaction between the enzyme(s) and flavor precursors (methyl, propyl, and propenyl derivatives of L-cysteine sulfoxide) occurs, resulting in the formation of flavour compounds. The odor of fresh onions is ascribed to thiosulfinates and thiosulfonates, while mono-, di-, and trisulfides present in the odor are considered secondary reaction products (see reviews by Whitaker, 1976, and Abraham *et al.*, 1976). The lachrymatory factor formed during onion slicing is also an important odor constituent. Its revised chemical structure as syn-propanethial-S-oxide, and a unifying proposal for its genesis were given by Block *et al.*, (1979). A part of the precursor during onion slicing is converted into cycloalliin, which is inert to the enzyme(s) and does not contribute to odor development.

In addition to sulfur compounds, the presence of propanal, its aldol condensation product, 2-methylpent-2-enal, and other carbonyl compounds in onion odor was emphasized by Freeman & Whenham (1974), while their genesis was outlined by Boelens *et al.*, (1971). An updated schematic of the genesis of major compounds responsible for the sensory characteristics of sliced onions is presented in Figure 16.

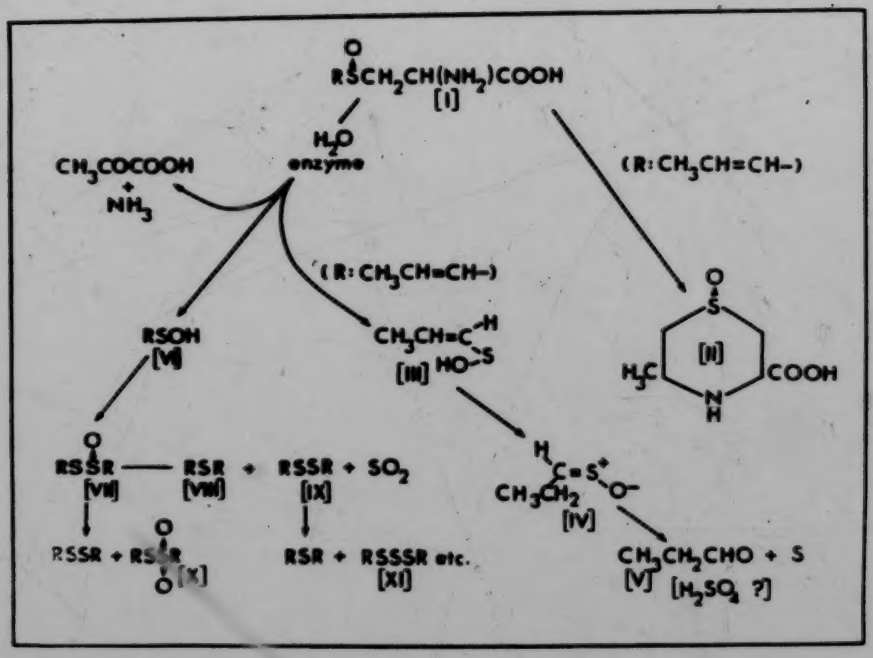


Figure 16. Genesis of some compounds responsible for sensory characteristics of *Allium cepa* L. (According to Abraham *et al.* 1976; Block *et al.* 1979). (I), 1-alkyl(alkenyl) cysteine sulfoxide; (II), Cycloalliin (3-methyl-1,4-thiazane-5-carboxylic acid-S-oxide); (III), alkyl(alkenyl) sulfenic acid; (IV), syn-Propanethial-S-oxide (lachrymatory factor); (V), Propanal; (VI), Sulfenic acid; (VII), Thiosulfinate; (VIII, IX, XI), Mono-, di-, and tri-sulfides; and (X), Thiosulfonate. R = CH_3-, C_3H_7-, or CH_3CH=CH-.

Numerous enzymes are involved in the biosynthesis of the aroma, and flavour precursors, in their breakdown to primary products, and perhaps also in the conversion of some of the primary products to sensory constituents or modifiers of sensory perception. However, only two have been investigated to the point where they can be described as entity (Whitaker, 1976). They are alliinase which has specificity for S-substituted L-cysteine sulfoxide, and γ-glutamyl transpeptidase which removes the γ-glutamyl group from γ-L-glutamyl trans-(+)-S-(1-propenyl)-L-cysteine sulfoxide to give the flavour, odor, and lachrymatory precursor.

Various methods have been advocated for measuring onion aroma. Spāre & Virtanen (1963) developed a semi-quantitative method in which 4 to 6 drops of plant extract adjusted to pH 6 to 7 were placed in a small weighing vial. Five milligrams of alliinase powder was added, the suspension stirred for 10 seconds, and the vial held tightly to the eye. Depending on concentration, the lachrymatory effect was perceived after 15 to 45 seconds. Currier (1945) advocated the use of volatile sulfur as a criterion of pungency and Kohman (1952) suggested the use of total volatile sulfur as an index of pungency and/or flavour.

Saguy *et al.* (1970) have suggested the use of the Chemical Oxygen Demand (COD) for estimation of the aroma and flavour components of onions. The procedure consists in oxidizing a distillate of the product with chromic acid and estimating the total volatile compounds colorimetrically. They reported a correlation coefficient of 0.98 between odor threshold and COD values for fresh onion; correlation was poor for dehydrated onion samples.

The olfactory threshold and the pyruvate content of onions developed enzymatically have a good correlation (r = 0.97), making this a suitable method for both fresh and dried onion samples when used under carefully controlled conditions (Schwimmer *et al.*, 1964). The pyruvate content is estimated colorimetrically after the 2,4-dinitrophenylhydrazone derivative has formed. Saghir *et al.* (1964) did not find a correlation between the aliphatic disulfide content and pyruvate, however, which is not surprising in terms of the continued reactivity of the primary products of the alliinase reaction.

Lukes (1971) has used the reaction of cysteine with thiosulfinates and thiopropanal S-oxide to estimate these initial products of alliinase action in crushed onion. The derivatives are separated on thin-layer plates. This method measures directly the primary products of enzyme action on the pungency, flavour, and aroma precursors. The method, while slow and laborious, could be quite useful for analysis of pungency, flavour, and odor potential. Freeman & McBreen (1973) have developed a rapid spectrophotometric method for determining thiosulfinates in hexane extracts of fresh, freeze-dried, and oven-dried onions. There was a good correlation between measured thiosulfinates and pyruvate concentration. Tewari & Bandyopadhyay (1975) introduced a thin-layer chromatography method for quantitative evaluation of the lachrymatory factor.

Gas chromatography has been used in the determination of the relative concentration of various flavour and aroma constituents in fresh, pickled, canned, boiled, fried, dehydrated or freeze-dried

onion (Bernhard, 1968; Boelens *et al.*, 1971; Tewari & Bandyopadhyay, 1977; Freeman & Whenham, 1974). Major differences in the relative proportions of some constituents in headspace chromatograms of fresh and dehydrated white onions were reported by Bernhard (1969). However, the conventional direct sampling method using a syringe is undesirable, since it leads the volatile sample containing a large amount of water to rapidly deteriorate the GC column. Thus, effective techniques to trap the headspace volatiles are required.

Several investigators (Dravnieks *et al.*, 197 ; Dirinck *et al.*, 1977) have reported on porous polymer techniques for the trapping of headspace volatiles. However, the usual procedures for sample recovery by solvent extraction or heat desorption from porous polymer followed by collection in a cold trap are troublesome and unsuitable for quantitative analysis.

1.2 Relative volatilities of some onion aroma components

Onion is about 80% water. Some understanding of the volatilities of its aroma components might be obtained by consideration of volatilities of these compounds in dilute aqueous solutions. A review of the literature revealed very little information in this area, especially in relation to sulfur-containing compounds.

Very significant work, however, was carried out by Butler *et al.* (1935), who studied water solutions of the homologous series of alcohols from methanol to octanol, and by Buttery *et al.* (1969, 1971), who studied the volatilities in dilute water solution of some members of the homologous series of alkanals, alkan-2-ones, and methyl alkanoates from C_3 to C_9 and some alkyl pyrazines and

unsaturated aliphatic aldehydes. Both groups found that the volatilities in the dilute water solutions gradually increased with increasing molecular weight. Pierotti *et al.* (1959) determined the activity coefficients (γ) of a number of organic compounds in water, using a variety of methods. They also determined the vapor pressure of some of the pure compounds, P, and from the calculation of the product γ and P were able to determine the volatilities of homologous series of paraffins, ethers, alcohols, and acids in dilute aqueous solution.

Kieckbusch & King (1979) used flame-ionization gas chromatography to determine equilibrium partition coefficients for C_1-C_5 acetates at high dilution between air and water, aqueous solutions of various carbohydrates, vegetable oils, and mineral oil. They found that partition coefficients between air and solutions of sucrose, maltose, and dextran (M, 90,000) increased sharply with increasing dissolved-solids content. For the disaccharide solutions this could be attributed qualitatively to a loss of free water due to hydration of sugar molecules. For solutions of maltodextrin, dextrin, and coffee solids, the acetates were held into solution more at the higher dissolved-solids contents, and the partition coefficient for pentyl acetate actually decreased with increasing concentration of dissolved solids. Partition coefficients between air and the oils were much lower and indicated an activity coefficient of about 0.7 for the acetates in coffee and peanut oils. Partition coefficients of a number of organic flavour compounds in safflower oil were reported by Buttery *et al.* (1973).

1.3 Volatiles retention during drying

It is primarily food aroma that distinguishes the flavour of one food from that of another, and aroma quality often determines the acceptability of a food. When water is removed from a food, the loss or retention of the food aroma is one of the major considerations in the design of the food processing operation (Bomben *et al.*, 1973).

Changes in aroma can occur during concentration and drying. These changes usually lower the quality of the products, but there are exceptions such as the removal of offensive amine odors from fish meal and mercaptan odors from raw milk. To minimize undesirable flavour changes, the temperature of concentration or drying is kept low, except for those cases where cooking produces a desirable flavour - for example, the development of dimethyl sulfide in tomato (Guadagni *et al.*, 1968), the production of maple syrup from maple sap (Underwood *et al.*, 1969), and the cooking of poultry meat (Pippen, 1967). However, in most cases it is important not to lose the natural aroma of the food product during concentration or drying.

For onion, which is consumed mainly on account of the volatile flavour components which are liberated when the tissues are

disintegrated, the quality is primarily determined by the concentration and composition of its odorous compounds.

Loss of components from onions on heating or drying has been studied by a number of researchers. Titov *et al.* (1964) established that on termination of freeze-drying of onions, ascorbic acid content was reduced by 50%; and that during air drying, ascorbic acid destruction was even greater. Copeman *et al.* (1947) reported that small losses of nitrogen and sulfur occur because of volatilization during drying. They came to this conclusion by measuring the total sulfur and nitrogen content of onions before and after dehydration. Differences in relative proportions of certain components in headspace gas-liquid chromatograms of raw, boiled and fried onion were reported by Boelens *et al.* (1971). Similar comparisons between fresh and dehydrated onion were made by Bernhard (1968, 1969) who reported total disulfide differences between fresh and dehydrated onions, of greater than 89%.

Model solutions have been extensively used for controlled studies of the factors affecting the loss of volatile aroma substances (Menting & Hoogstad, 1967a, b; Thijssen & Rulkens, 1968; Flink & Karel, 1970a, b; Rulkens & Thijssen, 1972 a,b; Flink & Karel, 1972; Thijssen, 1971; Kayaert *et al.*, 1975; Massaldi & King,

1974a,b; Lerici, 1976). These model solutions typically contain saccharides, such as sucrose, fructose, glucose or higher molecular weight dextrins, along with low concentration of simple volatiles aromatics, such as alcohols, ketones and esters. Menting & Hoogstad (1967a, b) studied the drying of single droplets of aqueous solutions of maltodextrin to which acetone had been added at low concentrations. They found that acetone was lost only during what is called the constant rate drying period. They also observed a decrease in volatile loss with increasing solid concentration. The retention was favorably influenced by decreasing the relative humidity of the air. A similar effect of drying conditions on volatile loss was found for slabs (Menting *et al.*, 1970).

Thijssen & Rulkens (1968) explained the anomalously high retention of organic volatiles by the selective diffusivity of water in aqueous solutions of organic solids at low water concentrations. They showed that the diffusivity of volatile organic compounds, if present in low concentrations, decreases much faster with decreasing water concentrations than the diffusivity of water. Below a critical water concentration the system becomes completely impermeable to organic volatiles. This critical moisture content is dependent on the molecular size of the volatile, the nature of the dissolved solids, and the temperature.

Flink & Karel (1970a) determined the retention values of several volatile compounds with a variety of mono-, di- and polysaccharideswhich were freeze-dried under identical conditions.

The ability to retain volatiles decreased in the order: disaccharide, monosaccharide, polysaccharide. These same authors (Flink & Karel, 1970b) also demonstrated that, in model solutions containing glucose and acetone, acetone retention after freeze-drying decreased as the initial glucose concentration decreased.

Studies on the retention of 2-propanol in aqueous suspensions of cellulose and starch (Chirife & Karel, 1973) revealed that starch gave much higher retentions than cellulose even at identical solids content and that increasing the amount of suspended starch and cellulose had a beneficial effect on the retention of 2-propanol, but the increase was much more pronounced with starch. Rulkens & Thijssen (1972b), who studied the retention of methanol, propanol, pentanol and acetone during spray-drying of aqueous solutions of malto-dextrin, demonstrated that retention increased with increased molecular size of the volatile, dissolved solids content, and drying rate. These findings are supported by the recent work of Smyrl & LeMaguer (1978) who studied the behavior of sparingly soluble volatile compounds of the terpene family during freeze-drying on a variety of substances, including gums.

Data on volatile retention in actual foods are limited. Sauvageot *et al.* (1969) reported results on volatile retention studies during freeze-drying of orange juice, and found that an increase in the dry matter content resulted in increased retentions for myrcene, limonene and pinene. However, in the same experiments ethanol exhibited the opposite behavior. A higher initial solids content has also been found to give substantially better retention

of volatile flavour species in apple juice (Chandrasekaran & King, 1971). In that study ethyl acetate, n-hexanol and n-hexyl acetate were chosen as representative apple volatiles.

Ofcarcik & Burns (1974) studied the effect of carbohydrate type, concentration of binary carbohydrate mixtures and sucrose hydrolysis on carbonyl retention in model systems and Bermuda onion juice, and reported that an increase in sucrose, glucose and lactose concentrations resulted in increased carbonyl retention. Bartholomai, *et al.* (1975) studied the effect of initial volatile concentration on an unidentified natural component in mushroom extract, benzaldehyde and oct-1-en-3-ol, and their results indicated than an increase in initial volatile concentration, at constant dissolved solids, results in a decrease in percentage volatile retention. Flink & Karel (1974) reported data on relative retention of coffee volatiles for various freezing and freeze-drying conditions and, once again, found that high initial solids content, high drying rate, low initial volatile concentration and a thin layer of sample resulted in higher retention. Massaldi & King (1974b) studied the retention of d-limonene during freeze-drying of orange juice and found that the presence of a stable cloud increased retention.

1.4 Aroma intensification

It is well known that cysteine is an important precursor in the formation of onion volatiles. Whitaker (1976), in his review, discussed the most important cysteine-containing compounds responsible for the final flavour development in onion. The enzyme alliinase acts on trans-(+)-S-(1-propenyl)-L-cysteine sulfoxide to produce thiopropanal-S-oxide, pyruvate and ammonia (Equation 1), and on (+)-S-methyl- and (+)-S-propyl-L-cysteine sulfoxides to produce the corresponding methyl methanethiosulfinate and propyl propanethiosulfinate (Equation 2).

$$CH_3CH = CHS(O)CH_2CH(NH_2)COOH \xrightarrow[+H_2O]{\text{alliinase}} [CH_3CH = CHSH = O] + CH_3COCOOH + NH_3 \quad (1)$$

S-(1-propenyl)-L-cysteine sulphoxide — 1-propenyl sulphenic acid — pyruvic acid

$$CH_3CH_2CH = S = O$$

thiopropanal S-oxide

$$2R\text{-}S(O)CH_2CH(NH_2)COOH \xrightarrow[+H_2O]{\text{alliinase}} RSS(O)R + 2CH_3COCOOH + 2NH_3 \quad (2)$$

S-alkyl-L-cysteine sulphoxide — thiolsulphinate

The thiosulphinates are rather unstable compounds. They can interact with cysteine to form stable disulfides (Small *et al.*, 1947).

Freeman & Massadeghi (1971), reported a positive correlation between sulfate fertilization and flavour strength of onion, which they attributed to increased availability of flavour precursors. The synthesis of cysteine from sulfides is well documented (Whitaker, (1976).

Inorganic sulfate is reduced to sulfide by an enzyme in the tissue (Equation 3).

$$SO_4^{2-} \xrightarrow[H_2O]{+\ 2H} SO_3^{2-} \xrightarrow[3H_2O]{+\ 6H} S^{2-} \qquad (3)$$

A sulfite reductase [hydrogen sulfide : (acceptor) oxidoreductase] has been purified from *Allium odorum* by Tamura (1965). The enzyme reduces sulfite to sulfide. Whether a separate enzyme is involved in reduction of SO_4^{2-} to SO_3^{2-} is not known. Cysteine is then probably synthesized in the following way from serine and sulfide (Equations 4 and 5).

$$\text{Acetyl-CoA + serine} \longrightarrow \text{O-acetylserine + CoA} \qquad (4)$$

$$\text{O-Acetylserine + } HS^- \longrightarrow \text{L-cysteine + acetate} \qquad (5)$$

The enzymes catalyzing these reactions have been isolated in pure form from *Salmonella* and been shown to exist partly as a complex of weight 309,000 (Kredich *et al.*, 1969).

Schwimmer and Guadagni (1967) found that using 1 mg/ml cysteine-HCl solution to rehydrate onion powder resulted in a 20-fold increase in odor intensity and alteration of gas chromatographic patterns of the volatiles. The compounds responsible for the observed effect were not investigated by the authors, though they commented that the reactions did not appear to be enzymatic in nature.

2. ANALYSIS

2.1 Experimental

2.1.1 Raw Material

The onions (*Allium cepa* L.) used were long-day, cooking-type Yellow Globe hybrid onions of cultivar Improved Autumn Spice, with an average moisture content of 87.1%. They were grown on sandy loam soil at the Alberta Horticultural Research Center, Brooks, Alberta.

The cultivar was sown April 15 at a row spacing of 60 cm. The seeds were sown by a push-type, cone seeder that also introduced granular 5% Diazinon into the seed furrow. Weed control was achieved by the use of a pre-emergence herbicide mixture of Dacthal and CIPC. Furrow and supplementary sprinkler irrigation maintained the soil moisture content close to 50% saturation. Onions were side-dressed with 27-27-0 at 112 kg/ha, while ammonium nitrate was later broadcast at 90 kg/ha as a top-dress, followed by sprinkler irrigation. Harvesting was done September 20-23, and the average yield was 37 tonnes/ha.

Commercially dehydrated, granulated white onions (with a declared flavour equivalent of 0.5 to 5 kg of raw onion) for use in meat products, canned foods, seasonings and soups, and for general institutional use, had maximum moisture contents of 4.25%, color (expressed as optical index) of 105, and size distribution (Tyler screen) of 2% on mesh size 32, and 5 and 1% through 100 and 150 mesh, respectively.

Laboratory dehydrated Yellow Globe onion slices with 7-9% moisture content were prepared by drying the slices with hot air at 80°C for 1 h followed by 60°C for an additional hour and then at 50°C for over 20 h, using a Vibro-Fluidizer (Niro Atomizer, Copenhagen, Denmark) with a 0.3 m^2 bed area.

2.1.2 Gas Chromatography - Mass Spectrometry

A Hewlett-Packard M5710A gas chromatograph was used, equipped with FID detectors and dual stainless steel columns. Columns of 2.4 m x 3.2 mm o.d. were packed with Chromosorb 101, a polyaromatic, cross-linked resin having a uniform rigid structure of distinct pore size. Separation by means of a liquid phase was done on 8% Carbowax 1500 coated on silylated (HMDS) Chromosorb W-AW-80/100 mesh and packed in columns of 9.14 m x 3.2 mm o.d. The column temperature for most runs was maintained at 60°C for 4 min and then programmed at 4°/min to 190°C. Isothermal runs were at 40, 50 and 80°C for 4, 8 and 16 min, with programming at 2 and 4°C/min to 140°C and holding at this temperature for 15 min. The carrier gas in all cases was N_2 at 25 ml/min. The injection port was maintained at 150°C and the detector temperature at 200°C. The area of the peaks was integrated by a Hewlett-Packard 3380 A electronic module.

A Hewlett-Packard M5933A mass spectrometer coupled with the 5710 A gas chromatograph was used for GC-MS analysis. Both retention time and mass spectral data were used for compound identification, in the latter case using only Chromosorb 101

packed columns, since column bleeding with Carbowax 1500 made the combined GC-MS analysis unreliable. MS parameters were as follows: inlet temperature, 250°C; ionization potential, 70 eV; ionization current, 300 uA; and scan speed, 3 s for a range of 25 to 400 m/e.

Pure sulfur organic compounds used in co-chromatography and mass spectra comparisons were provided by Polyscience Co. (Evanston, IL) and by Supelco, Inc. (Bellefonte, PA).

2.1.3 Headspace Sampling Procedures

Procedure I. The headspace volatiles were collected from a sealed system. Erlenmeyer flasks of 25 ml with Teflon stoppers having a centrally located rubber septum were used to incubate the onion sample. Fresh onions were sliced across the main axis to give 1 - 2 mm thick cylindrical slices. An 18 g sample was incubated in the flask at 40°C for 15 min and up to 3 h, and 3 or 10 ml headspace vapour was then withdrawn by a gas syringe and analyzed by GC.

Dehydrated samples were analyzed by the same method. However, preboiled distilled water was added to the samples and the contents shaken by a Burrell wrist action shaker (Burrell Corp., Pittsburgh, PA) with the incubation period limited to 15 or 30 min.

Procedure II. The volatiles were collected with a purging stream of N_2.

(a) The sampling apparatus was a 500-1000 ml Erlenmeyer flask fitted with a Teflon stopper and two glass tubes. One tube extending to near the bottom of the flask was used to continuously flush the onion sample with N_2, while the other exit tube had a Teflon end-tube fitted with a sealed gas syringe needle. Up to 200 g of fresh onion slices and various ratios of dehydrated onions to water (w/v) were used. The flask was incubated at 40°C and purged with N_2 at 15 ml/min for 15 min to 1 h prior to 3 or 10 ml of the volatiles being withdrawn.

(b) The injection procedure was simplified by the use of a six-way gas sampling valve (Varian Aerograph, Walnut Creek, CA). The gas valve was fitted with a 6 ml stainless steel sampling loop kept at room temperature during sampling and heated to 230°C during the injection period. The onion was slurried in a 300 ml stainless steel jar equipped with a blending set of blades and a two-port screw-cap which was connected by 3.2 mm o.d. stainless steel tubing to the N_2 supply and to the gas-sampling valve. In the sampling position N_2 at 30 ml/min passed through the onion sample and carried the volatiles to the valve through the sample loop into the atmosphere. When the purge time was completed after 15 min to 3 h and the valve turned to the injection position, the N_2 carrier gas was redirected to the loop to flush the trapped

volatiles into the column, while the purging N_2 was redirected straight to the atmosphere (Fig. 17).

Procedure III. Initially, the volatiles were concentrated in a trap of a porous adsorbent. The gas sampling loop in Procedure II was replaced by a 12 cm x 3.2 mm o.d. column packed with Tenax-GC of 80/100 mesh particle size. Tenax-GC, a porous polymer of 2,6-diphenyl-p-phenylene oxide was supplied by Applied Science Labs., Inc. (State College, PA). The volatiles were continuously flushed for 15-30 min with purging N_2 at 25-50 ml/min from 40 g of sliced or slurried sample held at 20, 40 or 70°C to the trap held at 0°C. The trap, which retained the adsorbed onion volatiles but not water, was then back-flushed into the GC column by N_2 carrier gas. At this time the Tenax-GC trap was heated to 230°C and kept at this temperature until the GC programming was completed.

2.1.4 Solvent Extraction Procedure

Onion volatiles were extracted in a Soxhlet apparatus using dichloromethane as a solvent. Fresh onion slices, 100 g, or dried onions, 3 g + 17.5 ml distilled water, were extracted for 3 h at 40-42°C with 250 ml solvent. The extract was concentrated to 1 ml in a vacuum flash evaporator kept at 40°C, and then used for GC-MS analysis.

2.2 Results and Discussion

The chromatogram of the volatiles of fresh onion slices extracted with dichloromethane is shown in Fig. 18. There were

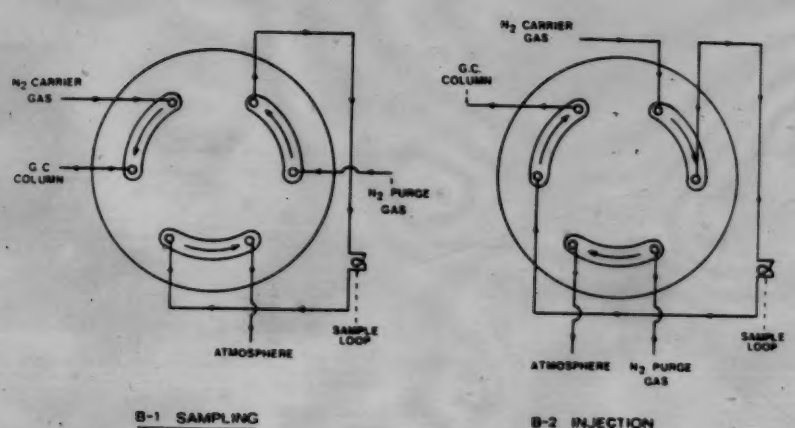


Figure 17. Injection valve used in headspace analysis by Procedure IIb. The sampling and injection positions of the valve are shown.

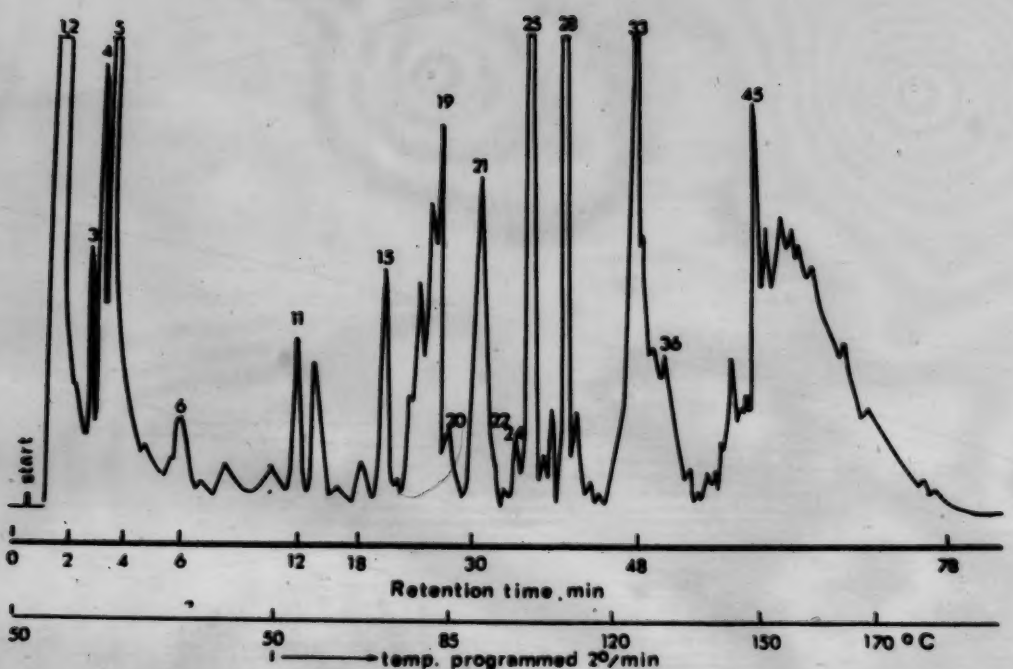


Figure 18. GL-chromatogram of onion flavours extracted with dichloromethane. Separation column used: Carbowax 1500. For peak designation see Table II.

close to 60 resolved constituents, 13 of which were major, with the rest being intermediate and minor constituents. The lowest retention time was for oxygen derivatives, mostly carbonyls and thiols. Saturated disulfides had a retention time higher than 6 min, while the highest retention time was for unsaturated disulfides and trisulfides. The latter were eluted near the end of the chromatograms. The identities of major peaks, based on retention time, co-chromatography and MS data, are listed in Table II.

Dehydrated onions had similar chromatograms. However, relative to other peaks, the 3,4-dimethylthiophene peak area in dehydrated samples increased while that of propyl propenyl disulfide decreased. This finding corroborates those of Boelens *et al.* (1971) that certain disulfides serve as thiophene precursors when onions are processed at higher temperatures.

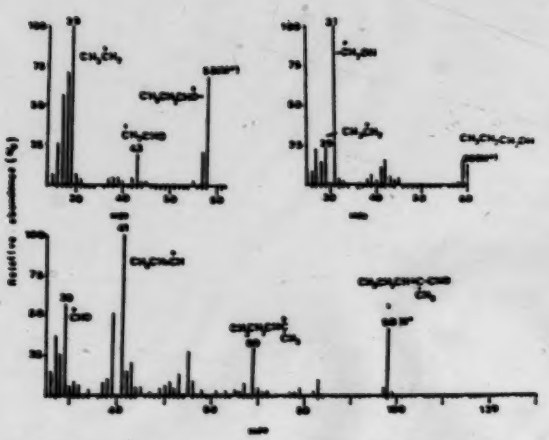
Fresh onion slices, dehydrated onions, or onion oils obtained by solvent extraction or steam distillation contain a great abundance of flavour constituents. Dimethyl disulfide, methyl propyl disulfide and dipropyl disulfide, as well as corresponding trisulfides, have been identified in steam distilled oil (Carson & Wong, 1961). Brodnitz *et al.* (1969) and Brodnitz & Pollock (1970) listed 17 constituents, all di- and trisulfides except for a single dimethylthiophene, while Boelens *et al.* (1971) found a total of 45 volatile constituents. Abraham *et al.* (1976) reviewed a total of 74 compounds identified so far in fresh and processed onions.

Table 11. Compounds identified in solvent extract of fresh onion slices.

Peak No.	Compound[1]
1	methanethiol + ethanal
2	propanal
3	propanethiol + 2-methylbutanal
4	methanol + 2-methylpentanal
5	ethanol + propanol
11	dimethyl disulfide
15	2-methylpent-2-enal
19	methyl propyl disulfide
20	3,4-dimethylthiophene
21	methyl cis-propenyl disulfide
22	methyl trans-propenyl disulfide
23	dimethyl trisulfide
24	isopropyl propyl disulfide
25	dipropyl disulfide
28	propyl cis-propenyl disulfide
33	propyl trans-propenyl disulfide
45	dipropyl trisulfide

[1] *Identification was based on retention times, co-chromatography and MS-data.*

In Fig. 19, MS-fragmentation patterns are presented for propanol, propanal and 2-methylpent-2-enal. Data for propanethiol and two disulfides are given for comparison purposes. The mass spectra of thiols were dominated by peaks corresponding to hydrocarbon fragments $C_nH_{2n-1}^+$ and C_nH_{2n+1}. Loss of HSH from M^+



Parent peak (M^+)	Base peak	m/e Relative abundance (%)								Compound
76	41	47 90.4	43 84.6	42 81.1	76 67.3	27 51.4	39 48.3	45 40.1	46 26.7	Propanethiol
122	43 or 80	43 100	27 90.1	122 82.4	41 81.3	28 71.4	45 70.3	39 50.5	46 48.4	47 44.0	Methyl-n-propyl disulfide
150	43	41 53.1	27 52.3	150 29.3	39 29.0	108 23.0	45 21.4	66 13.7			Di-n-propyl disulfide

Figure 19. Mass spectral data for some volatile onion constituents.

gave rise to the fairly abundant hydrocarbon radical ion C_nH_{2n}. Aliphatic sulfides displayed more abundant molecular ions and sulfur-containing fragment ions than the corresponding thiols, but the hydrocarbon peaks were still predominant in the spectra. Mass spectra of aliphatic thiols and sulfides and their mechanism of fragmentation were described in detail by Levy & Stahl (1961). Unique mass spectral fragmentation patterns of 1-propenyl-containing thiols, sulfides and disulfides, and thiopropanal-S-oxide were described by Nishimura *et al.* (1973).

Fig. 20 shows typical chromatograms from two headspace sampling procedures applied to fresh onion slices incubated for 30 min. A 3 ml sample of headspace volatiles, withdrawn from the closed system (Procedure I) revealed close to 13 major and intermediate constituents, the major ones being propanal, propanethiol, 2-methylpentanal, propanol, 2-methylpent-2-enal, methyl propyl disulfide, dipropyl disulfide, and propyl cis- and trans-propenyl disulfides. When 10 ml headspace volatiles were collected from a stream of purging N_2 (Procedure II), the chromatogram was made up of essentially the same compounds but much more intensified, and in addition 4 new peaks were detected while 2 previously found constituents were absent.

Averages of three replicates of the areas under the peaks obtained by Procedure II (a or b) and the dependence on incubation time of onion slices are shown in Table 12. Most peak areas increased with increasing incubation time, reaching a maximum at about 3 h and then decreasing. Prolonging the

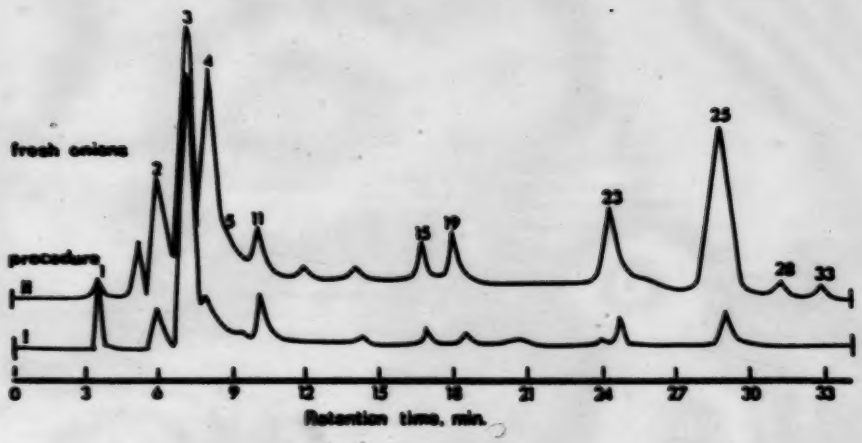


Figure 20. GL-chromatograms of the volatiles of fresh onion slices obtained by applying headspace sampling Procedures I and II for a duration of 30 min. For peak designation see Table 11.

Table 12. Effect of sampling time on the development of fresh onion volatiles collected by Procedure II and separated by GC on Carbowax 1500 coated columns.

Compound	Peak area in cm^2 from 10 ml of vapour injected after incubation for					
	30 min	85 min	3 h	4 h	5.5 h	7 h
pre-propanal peaks	0.79[1]	3.54	5.18	3.27	2.71	2.04
propanal	10.97	18.32	23.33	13.87	9.43	6.42
propanethiol (+ 2-methylbutanal)	1.99	19.43	24.97	3.45	2.90	2.60
unknown	0.25	0.09	-	-	-	-
2-methylpentanal (+ methanol)	0.10	0.35	0.80	0.84	0.85	1.12
propanol	0.11	0.33	0.71	0.79	0.71	0.80
dimethyl disulfide	-	0.35	0.21	-	-	-
2-methylpent-2-enal	0.27	0.92	1.52	1.06	0.54	0.32
methyl propyl disulfide	0.30	2.13	1.69	0.32	0.19	0.08
dipropyl disulfide	2.29	6.34	9.25	1.71	0.67	0.39
propyl cis-propenyl disulfide	-	-	0.20	-	-	-
propyl trans-propenyl disulfide	0.16	0.25	0.37	-	-	-
Total	17.31	52.00	68.26	25.29	18.05	13.77

[1] *All the peak area figures are means of three replicates and were obtained from 200 g of fresh onion slices/500 ml flask held at 40°C with N_2 purge gas flow at 20 ml/min. The coefficient of variation was < 5%.*

incubation from 30 min to 3 h caused a nonuniform 2.1 to 6.1-fold increase in peak areas for propanal, methyl propyl disulfide and dipropyl disulfide, while propanethiol showed the highest increase (12.5-fold). The sum of all the peak areas was a maximum of 68.3 cm^2 after 3 h incubation time. By prolonging this time the sum decreased rather abruptly. An additional hour of incubation brought about a decrease in volatiles of 2.7 times, while a 5-fold decrease in area was obtained after a further 4 h incubation. These findings proved that, regardless of the procedure (II a or b), the results are dependent on the sampling time.

Dehydrated Yellow Globe onions had chromatograms as shown in Figure 21. For laboratory dehydrated samples, when Procedure I was applied and the onion to water ratio was increased from 0.11 to 1.80 (w/v), the number of constituents detected increased from 9 to over 20, while the sum of all the peak areas rose from less that 5 to 45.6 cm^2. The dehydrated onion chromatograms retained nearly all the major volatile constituents of fresh onions. However, their amounts were less, while the constituents with retention times between 12 to 15 min and dipropyl disulfide were below their detection limit at a rehydration ratio of 0.11, while at a ratio of 1.80 these peaks and several new ones were readily revealed. Chromatograms of commercially dehydrated onions were similar to those of laboratory dried onions after a 0.11 ratio dehydration. Also, when onions were rehydrated in a ratio of 0.11, incubated for 30 min and then

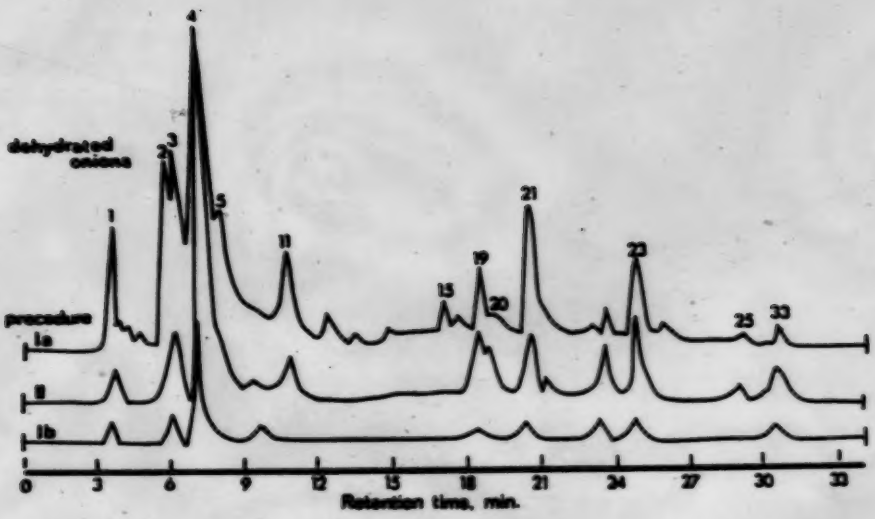


Figure 21. GL-chromatograms of dehydrated onion volatiles obtained by applying headspace sampling Procedures I and II for 30 min. For peak designation see Table II.

assayed by Procedure II, the chromatograms were similar to those of Procedure I.

Chromatograms of fresh and dehydrated onion volatiles trapped on Tenax-GC by Procedure III are shown in Fig. 22. The volatiles collected from fresh onion slices during 15 min incubation and then separated on a Carbowax 1500 coated column revealed a total of 28 peaks, with major ones being propanal, propanethiol, 2-methylpent-2-enal, methyl propyl disulfide and dipropyl disulfide. Unsaturated disulfides and trisulfides were not present. Nevertheless, the procedure, though it simulated the closed system of Procedure I, was still able to reveal 15 additional constituents. Similarly, Procedure III was superior to Procedure II. Chromatograms of dehydrated onion in an amount equivalent to the fresh weight assayed by Procedure III revealed a total of 14 well-defined peaks which coincided with those of Procedure II (a or b). However, the relative proportions of peak areas differed substantially in Procedure III.

The Tenax-GC trapping procedure was used to study the variation in the composition of volatiles with extent of disintegration of the onion tissue. Fresh onion was diced, sliced, or sliced and blended. In addition onion slices were blended with and without water. The samples were incubated in the normal manner, and trapped for a period of 15 min and then separated on a Chromosorb 101 column. The results are presented in Table 13. A comparison of peak areas revealed that with

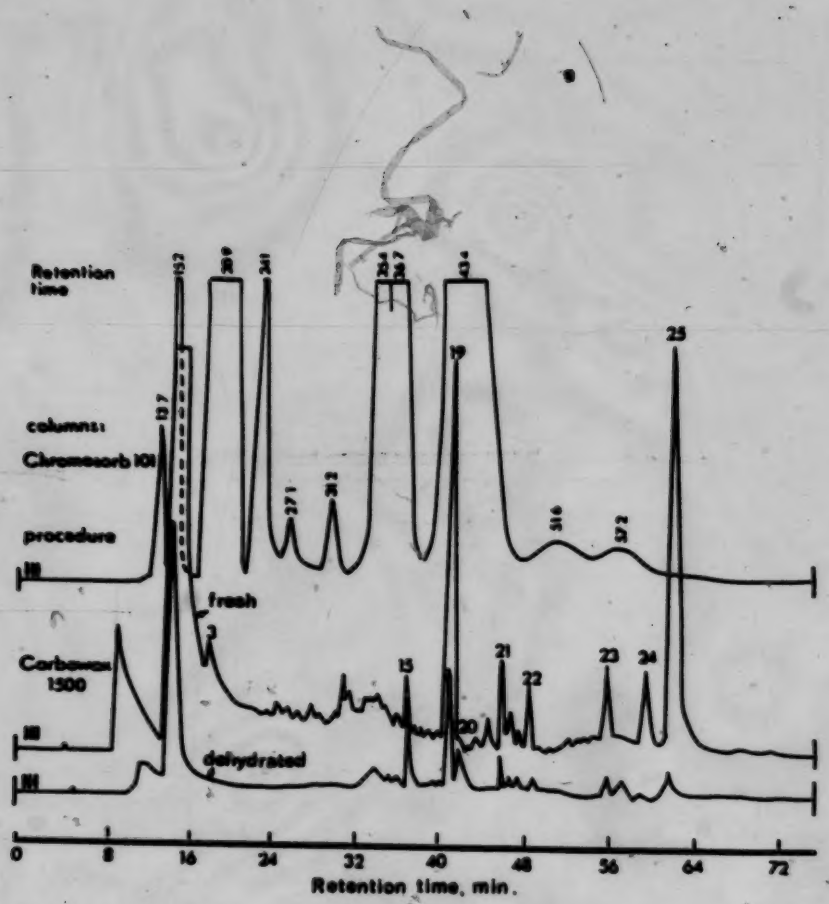


Figure 22. Chromatograms of fresh and dehydrated onion volatiles concentrated previously on a Tenax-GC trap for 15 min.

Table 13. Variation in headspace GC peak areas of fresh onions with the extent of sample disintegration.

Peak retention time [1]	Compound	Disintegration extent					
		Diced	Sliced	Blended	Sliced-1 [2]	Sliced-2 [3]	Sliced-3 [4]
13.7	propanal	4.57	10.83	13.92	10.24	3.92	3.10
15.2	propanol	1.71	5.13	8.99	11.52	6.91	1.53
20.9	propanethiol	265.33	697.44	857.93	414.28	502.82	246.66
24.1	2-methylpentanal	36.41	4.31	5.20	3.54	0.89	1.95
27.1	unknown	5.52	2.32	1.17	-	0.02	0.45
31.2	2-methylpent-2-enal	0.96	30.80	37.88	2.23	15.40	2.80
35.4	methyl propyl disulfide	182.33	25.11	57.30	19.76	39.31	10.93
36.7	unknown	-	20.55	-	-	-	16.83
43.4	dipropyl disulfide	308.13	156.18	91.65	5.23	66.39	32.06
	Total	804.96	1003.0	1074.04	466.80	635.66	316.31

[1] *The volatiles were trapped on Tenax-GC for 15 min and then separated on a Chromosorb 101 GC column.*
[2] *Sliced in sampling jar, blended for 10 sec, then the jar was closed and connected to the Tenax-GC trap.*
[3] *Sliced in sampling jar, 100 ml of water added, jar closed and connected to the trap, then blended for 10 sec.*
[4] *Sliced in sampling jar, 100 ml of water added, jar closed and connected to the trap, no blending.*

onions sliced instead of diced, the release of volatiles was enhanced by close to 25%. Most of the major volatile constituents increased in amount. Propanal, propanol and propanethiol peak areas increased by 55, 67 and 62%, respectively. On the other hand, a few constituents decreased in amount, most noticeably dipropyl disulfide (49%) and 2-methylpentanal (98%). The results suggested that as the extent of disintegration of tissue increased, more volatiles were released and less propanethiol was converted to its disulfide. However, when disintegration was as extensive as in the blended samples, the additional rise of total volatiles was only 7.1%. Again, propanethiol was enriched at the expense of the dipropyl disulfide, and there was a noticeable enrichment of methyl propyl disulfide.

Volatiles collected from a sample blended for 10 sec with the sampling jar open and connected to the Tenax-GC trap only after blending was completed showed a total loss of volatiles amounting to 56.5%. Two major constituents were particularly affected: propanethiol and dipropyl disulfide. Their losses were 51.7 and 94.3%, respectively. There was also a substantial loss of 2-methylpent-2-enal and methyl propyl disulfide.

Addition of water to onion slices decreased the amount of volatiles collected. Thus, sliced onions in water released only one third, while sliced and blended samples in water released slightly more than half of the volatiles usually released in the absence of water.

The effect of temperature on release of volatiles was also investigated. The optimum onion enzyme activity was assumed to be at 40°C. Temperatures of 20 and 70°C were also assayed since they are often encountered in household and institutional markets. The released volatiles incubated at these temperatures were continuously flushed to the Tenax-GC trap (with an N_2 stream) and then analyzed on Chromosorb 101 columns. At all temperatures the number of volatile constituents was the same, however, the amount of volatiles greatly increased with temperature. The peak area for propanethiol increased by 52% for a rise from 20 to 40°C and by 84% for a rise from 40 to 70°C. Dipropyl disulfide, as well as some other peak areas, had close to a 90% increase in the range of 20 to 40°C and slightly less than 60% with an additional rise from 40 to 70°C. When the difference between the total and control pyruvate values of fresh onion slices heated at 70°C for 15 minutes were determined according to Freeman and Mossadeghi (1971), the pyruvate data obtained corresponded to an 80% loss of onion enzyme activity. Hence, a rise in flavor constituents of onions at higher temperatures cannot be ascribed to enzyme activity but rather to their solubility decrease in water and to an overall increase in vapor pressure of the constituents.

The sampling procedures for headspace volatiles, when compared to solvent extraction procedures, do not reliably quantify the higher boiling constituents of onions. However, since the volatiles found in the headspace are probably those experienced by the consumer, and because of its simplicity and ability to avoid artifacts, analysis of the headspace was preferred in this study.

A modified version of sampling Procedure 1, as applied in this study, was used by Bernhard (1968), Boelens *et al.* (1971) and Freeman and Whenham

(1974). However, as observed by the latter authors, some of the GC findings related to fresh and dehydrated onions were difficult to reconcile. A linear relationship between total GC peak area and onion sample weight held only up to 2 g. As shown in the present study, the GC method is sensitive, but for reproducibility of results, standardization of the sampling procedure is a prerequisite. The extent of disintegration by a Waring blendor in a sealed system, incubation temperature of 40°C, and a 15 or 30 minute sampling time were preferred. Also, a standardized dehydrated onion rehydration ratio of 1.8 w/v was found to be satisfactory. Preliminary concentration of headspace volatiles by trapping in Tenax-GC provided a simple procedure for following the changes of both major and intermediate constituents. All these findings stress the need for a specified common sampling procedure by headspace GC methods for onion flavor assessment to compare data on the effects of processing, storage, variety, fertilization and irrigation on onion flavor quality.

3. RELATIVE VOLATILITIES

3.1 Experimental

The organic compounds used were obtained from reliable commercial sources (Aldrich Chemical Co., Milwaukee, WI. and ICN K & K Labs Inc., Plainview, N Y) and checked for their purity by gas chromatography (GC) before use. The water was distilled and then boiled to remove volatile impurities and air. The GC apparatus was a Hewlett Packard Model 5710A with dual flame ionization detection. The dual columns were 2.44 m x 3.175 mm o.d. stainless steel packed with Chromosorb 101, 80/100 mesh and operated at temperatures ranging from 80°C for ethanal to 180°C for dipropyl and diallyl disulfides. Nitrogen was used as the carrier gas and the flow rate was 30 ml/min. Hydrogen flow rate was 25 ml/min and air flow rate 275 ml/min. Hamilton gas-tight and conventional glass cylinder and barrel type syringes were used to inject the vapor and liquid phases into the GC unit.

For the determination of the partition coefficient, a volume of the chemical under test which would give a concentration of 5 - 500 ppm (w/w) was added to 135 ml of boiled distilled water at room temperature in a 270 ml Teflon bottle. The bottle was closed immediately, shaken vigorously and placed in a 25°C constant temperature water bath for 15 min or more to equilibrate. The needle of a 2.5 ml gas-tight syringe was then pushed through the rubber cap of the bottle and the headspace gas forced into the syringe by squeezing the bottle. The vapor phase sample, 2.0 - 2.5 ml, was then injected directly into the GC apparatus through the silicon rubber septum injector. Solution samples, 2.5 - 10.0 µl, were taken out of the bottle, used for the vapor samples, and injected

immediately into the GC unit. Solution and vapor samples were injected alternately so that a change in the concentration of the solution due to vapor removal would be compensated for. The injector temperature was maintained at 200°C to ensure rapid vaporization of the solution, and the detector temperature was 250°C. The air/water partition coefficients were determined as k = (weight of solute per ml of air)/(weight of solute per ml of solution) at 25°C and 1.0133×10^5 Pa.

The GC peaks area of the solution and vapor peaks were measured with a Hewlett Packard 3380A electronic integrator. The injection of both solution and vapor allows the cancelling out of the GC peak area to weight conversion factors and simplify the calculation to

$$k = \frac{\text{Peak area (vapor)/vapor sample volume}}{\text{Peak area (liquid)/liquid sample volume}} \qquad (6)$$

For each compound, k was calculated as the average of at least four determinations. From the values of k the relative volatility of each compound, i.e., the ratio of the volatility of that compound and the volatility of water at the same temperature, was calculated directly as:

$$\alpha_{io} = \frac{y_i/x_i}{y_o/x_o} = k \cdot \left(\frac{RT\rho_W^L}{M_W P_W^S}\right) = k \cdot \frac{\rho_W^L}{\rho_W^G} = k \cdot 4.3333 \times 10^4 \qquad (7)$$

where y_i and y_o are, respectively, the concentrations in mole fraction of aroma component and water in the vapor in equilibrium with the liquid phase in which their concentrations are x_i and x_o; P_W^S, saturation pressure of pure water at 25° = 3.169×10^3 Pa; T = 298.16 K; ρ_W^L, density of liquid H_2O = 997.11 kg/m^3; R, gas constant = 8.3143×10^3 J/K k mole; M_w, molecular weight of water = 18; and ρ_W^G, density of water vapor at 25°C = 2.3062×10^{-2} kg/m3.

3.2. Results and Discussion

Table 14 lists the relative volatilities found for the compounds examined together with the partition coefficients, boiling points and molecular weights. The air/water partition coefficients are given to allow for the rapid calculation of an unknown concentration in one medium when the concentration is known in the other medium. The boiling points and molecular weights have been taken from the Handbook of Chemistry and Physics (1973).

Upon examining the results in Table 14, it is immediately obvious that the volatility of the compounds examined varied appreciably. Propanethiol, for instance, was about fifteen thousand times more volatile than methanol and over one hundred times more volatile than propanal. Also, dipropyl disulfide was four times less volatile than methyl propyl disulfide and over two and one-half times less volatile than diallyl sulfide. Less obvious is the fact that, while the volatility of aldehydes and alcohols increased gradually with the molecular weight and boiling point, the volatility of the sulfur-containing compounds followed the opposite trend. This may be due to their difference in solubility in water, as well as to the unique properties of the sulfur atom. The introduction of two double bonds, dipropyl disulfide vs. diallyl disulfide, increased the volatility by two and one-half times. This may be due to the partial shifting of the electron pair and, hence, to the lack of hydrogen bond between water and sulfur.

There are no published volatility data of sulfur-containing

Table 14. Relative volatilities, air/water partition coefficients, molecular weights and boiling points of fourteen onion volatiles.

Compound	Molecular weight[a]	Boiling point[b] (°C)	Air/water partition coefficient (k)	Relative volatility (α_{io})
Propanethiol	76.2	67.5	$4.48 \pm 0.25^{c} \times 10^{-1}$	19,413
2,5-Dimethylthiophene	112.2	136.7	$1.08 \pm 0.20 \times 10^{-1}$	4,680
Methyl propyl sulfide	90.2	95.5	$9.37 \pm 0.75 \times 10^{-2}$	4,040
Dimethyl disulfide	94.2	109.0	$4.69 \pm 0.02 \times 10^{-2}$	2,032
Dipropyl disulfide	150.3	193.3	$2.25 \pm 0.20 \times 10^{-2}$	975
Allyl methyl sulfide	88.2	92.0	$8.05 \pm 0.65 \times 10^{2}$	3,488
Diallyl sulfide	114.2	139.0	$5.66 \pm 0.34 \times 10^{-2}$	2.453
Diallyl disulfide	146.0	--	$5.38 \pm 0.50 \times 10^{-2}$	2.331
Ethanal	44.1	20.8	$2.48 \pm 0.25 \times 10^{-3}$	107
Propanal	50.1	48.8	$3.43 \pm 0.25 \times 10^{-3}$	149
Methanol	32.0	64.9	$3.02 \pm 0.50 \times 10^{-5}$	1.3
Ethanol	46.1	78.5	$6.52 \pm 1.00 \times 10^{-5}$	2.8
1-Propanol	60.1	97.4	$10.81 \pm 0.87 \times 10^{-5}$	4.7
2-Propanol	60.1	82.4	$19.61 \pm 1.60 \times 10^{-5}$	8.5

[a, b] *Handbook of Chemistry and Physics (1973).*

[c] *Standard deviation.*

compounds with which to compare the figure obtained in this work, but a comparison of the volatility figures for ethanol and propanal with those of Buttery *et al.* (1969) was made and the difference was found to be within the experimental error.

The high relative volatility values obtained for some of the most important onion flavouring components (e.g., propanethiol, dipropyl disulfide) indicates that these compounds will reach the olfactory sensors more abundantly when fresh onion is cut and that the potential loss during dehydration is very high. This is because flavour components in liquid foods, or foods with low dry matter content, undergoing drying have the tendency to evaporate much faster than water. After partial evaporation of water, if the vapor removed is in equilibrium with the liquid and if there is no concentration gradient in the solution, the retention of a flavouring component, i, can be expressed by the following expression (Menting *et al.* 1970):

$$\frac{M_i}{M_{io}} = \left(\frac{M_W}{M_{Wo}}\right)^{\alpha_{io}} \qquad (8)$$

where M_{io} and M_{Wo} are the amounts of flavouring component and water initially present in the solution and M_i and M_W are the amounts left after partial evaporation. According to this equation, with α_{io} values of the magnitude shown in Table 14 , drying of onion will result in a very rapid depletion of the flavour. This can be illustrated by the following example. The retention of dipropyl disulfide, a compound with rather intermediate volatility will be 5.6×10^{-3}% when only 1% of water is evaporated, and 2.4×10^{-43}%

when 10% of the water is evaporated. The retention of 1-propanol, a compound with low volatility, will be much higher than dipropyl disulfide, 95% and 61% for 1% and 10% of the water evaporated, respectively. Fortunately, equation (8) holds only if the evaporation at the surface is not limited by the mass transport in the liquid phase. In the dehydration of onion this condition can only be fulfilled at the very beginning of drying. At low water concentrations the diffusion coefficients in the liquid and solid phases are very low (Thijssen, 1971) and, thus, the resistance to mass transfer in these phases becomes much greater than that in the gas phase, hence, even after over 95% of the water has been removed from onion slices there is still sufficient flavour to give dehydrated onions their well-known flavour.

4. MOVEMENT OF SELECTED VOLATILE COMPONENTS

4.1 Experimental

The onions were those used for the dehydration study and of the White Globe type (cv. Improved South Port White Globe). The dry matter content of the white onion was 21.11%, as compared to 12.87% for the Yellow Globe type.

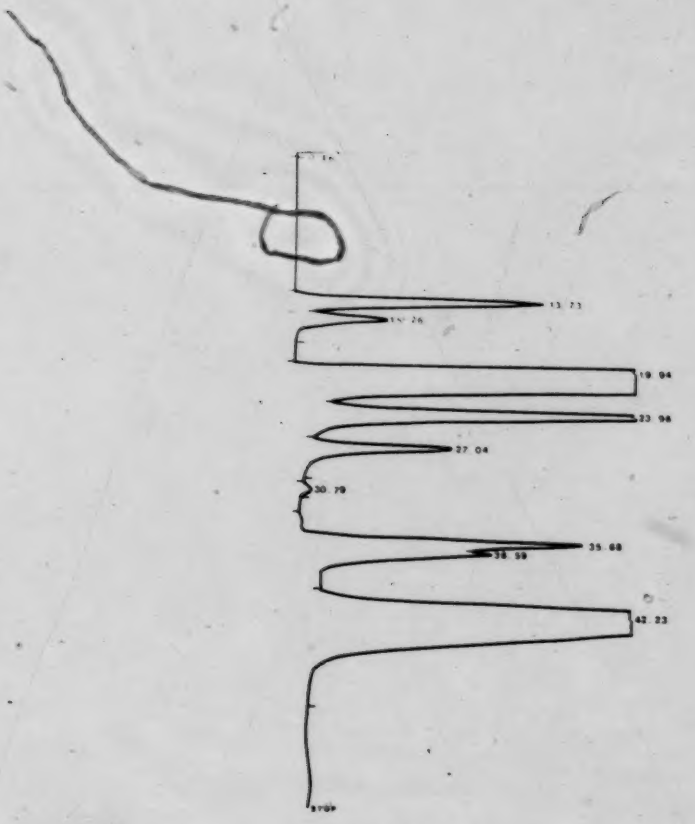
Volatiles present in fresh and dehydrated onion were measured using the gas-entrapment, on-column trapping technique described previously. The dried onion was crushed and screened before analysis, and only the fraction greater than 1.7 mm and smaller than 4.0 mm in length was used.

The location of volatiles in onions was determined with a simple optical microscopic technique and by a sensory panel. For the microscopic technique, bulbs of onion were cut into blocks to fit a hand microtome equipped with a razor blade (Scientifice Supply, Madison, WI). Ten to 15 sections of about 200 μm thickness were then cut and transferred to microscope slides. The slices were spotted with 1% aqueous silver nitrate solution and photographic images of different fields were recorded at 50X magnification. Enlarged photomicrographs of 150X magnification were then developed. The images were taken with an Olympus Model BHA microscope equipped with an Olympus camera (Olympus Optical Co. Ltd., Tokyo, Japan). For the sensory evaluation, different portions of the onion scale were removed (narrow portion containing the vascular bundle region, section without vascular bundle, outer epidermis) and evaluated for typical onion flavor by two individuals who had experience in judging onion.

4.2. Results and Discussion

A typical gas liquid chromatographic scan of fresh South Port White Globe onion is shown in Figure 23. The identified compounds are presented in Table 15, with their retention times (peak numbers) of Figure 23. The tabulation notes the certainty of identification. A positive identification represents agreement with published mass spectra data and with retention time of pure compounds on the Chromosorb 101 column. Figure 15 shows a chromatogram of the compounds present in dehydrated Improved Autumn Spice onion. This chromatogram was obtained from a mixture of 9.1 g of onion with 29.1% moisture content, and 40.9 ml H_2O. This mixture is equivalent to 50 g of fresh onion. The qualitative composition of the compounds in fresh white globe and fresh yellow globe type onion was essentially the same as that of the dehydrated product.

For the retention of volatile compounds during drying of liquid foods and model systems two basic mechanisms have been proposed. The selective diffusion concept (Thijssen & Rulkens, 1968; Menting *et al.*, 1970), and the microstructure concept (Flink & Karel, 1970a,b; 1972). According to the selective diffusion concept, the transport of both water and volatile compounds in a drying liquid food is governed by molecular diffusion. The diffusion coefficients of water and of volatiles decrease strongly with decreasing water concentration; the decrease of the diffusion coefficient of volatiles, is, however, much sharper than that of the diffusion coefficient of water. Some time after the beginning of the drying process the interfacial water concentration in the liquid food drops to such a low value that a "dry skin" is formed.



AREA %

RT	TYPE	AREA	
46		22	.000 154 4
13.73		282488	1.981
15.26	M	110429	.775 2
19.94		10309482	72.37
23.94	T	477499	3.352
27.04	TM	167082	1.173
30.79	T	9918	.069 63
25.68	T	364835	2.561
36.59	TM	288178	1.967
42.23		2243815	15.74

HP 3380A
RLY OFF
RMVM 10

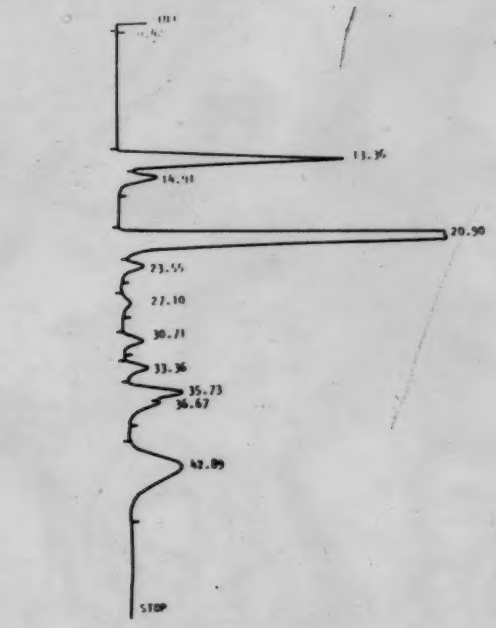
STOP 60
ATTN 0

REJECT OFF

Figure 23. Gas chromatograms of vapour of fresh South Port White Globe onions.

Table 15. Compounds identified in headspace of sliced onion with a Chromosorb 101 column.

Retention time	Compound	Identification	
		Positive	Tentative
13.73	Propanal	+	
15.26	Propanol	+	
19.94	Propanethiol	+	
30.79	2-methyl-2-pentenal		+
35.68	Methyl propyl disulfide	+	
42.23	Dipropyl disulfide	+	



RT	TYPE	AREA	AREA %
.42		42	.007 79
13.36		275200	18.28
14.91	M	51611	3.428
20.90		761751	50.6
23.55	M	31303	2.079
27.10		15581	1.035
30.71		26512	1.761
33.36		28026	1.865
35.73	M	70648	4.691
36.67	M	43318	2.877
42.89		201487	13.38

HP-3380A
SLV OFF
RF/M .10

STOP 60
ATTN 8

REJECT OFF

Figure 24. Gas chromatogram of vapour of partially dehydrated Improved Autumn Spice onion.

At this low water concentration the diffusion coefficients of the aroma components are so much lower than that of water, that the dry skin is virtually impermeable to aroma components. The microstructure concept has been used for the description of aroma retention in freeze-drying. It postulates that, during freezing and subsequent drying, microregions of high solute concentrations are formed in which aroma molecules may be entrapped.

The relationship between moisture content and 'total' onion volatile retention is shown in Figure 25. This shows that during the initial drying phase the volatiles escape rapidly. Once a moisture content of 70-75% has been reached, the rate decreases, and from a moisture content of 35-40% onward hardly any more volatiles are lost. Total volatile retention is, however, misleading, since it reflects the behaviour of the components present in higher concentration, and it is the concentration and/or the odor threshold of the individual volatiles as well as the proportions of the mixture components that determine the quality of the food product.

Figure 26 illustrates the percent retention of propanol, dipropyl disulfide, methyl propyl disulfide and propanethiol as a function of moisture content. A comparison between these four curves shows that each volatile behaves differently during drying. To be noted in the figure is the different moisture content at which these four compounds were locked in. Propanethiol retention leveled off at about 70% moisture content, methyl propyl disulfide at about 50% moisture content, dipropyl disulfide at about 25%

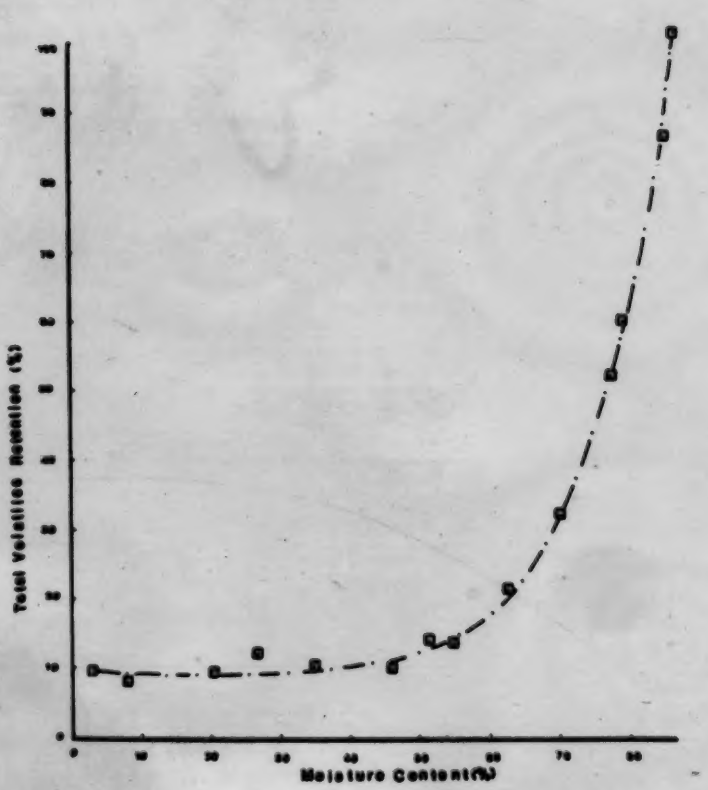


Figure 25. Retention of 'total' onion volatiles in percent of the initial amount in drying onion slices as a function of the moisture content. Drying conditions: 50°C and 8.1 m^3/min air flow rate.

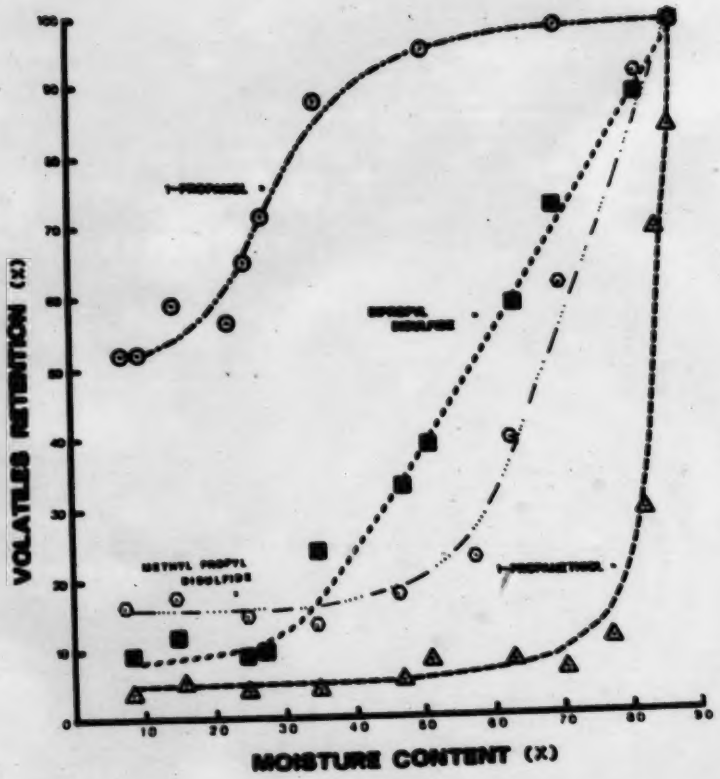


Figure 26. Propanol, dipropyl disulfide, methyl propyl disulfide and propanethiol content in percent of the initial amount in drying onion, as a function of moisture content of the onion slices dehydrated at 25°C.

moisture content and propanol at even lower moisture content. This behavior was observed under many different drying conditions, and seems to imply that the loss of each compound ceases at a moisture content which is specific to that compound and, perhaps, to onion only.

The relative concentration of these four compounds in the fresh onion, as estimated from the peak areas, was approximately 100 for propanethiol, 25 for dipropyl disulfide, about 5 for methyl propyl disulfide and 1 for propanol. From an analysis of the published results (Chirife *et al.*, 1973; Bartholomai, *et al.*, 1975) on volatile retention vs. initial volatile concentration, it appears that the final retention of compounds having similar properties can be approximately predicted by assuming that the final retention varies linearly with the logarithm of the initial concentration.

If we take propanol as a base and apply this approximate proportionality to the results presented in Figure 26 we find that the calculated final retention for propanethiol is about 4% as compared to the observed retention of 5%. The calculated retention for dipropyl disulfide is about 17%, as compared to the observed retention of 8%, and the calculated retention for methyl propyl disulfide is 33%, as compared to the observed retention of about 16%. From the basic properties of these compounds (Table 16), it can be seen that propanethiol is more similar to propanol than are dipropyl disulfide or methyl propyl disulfide. This likely results in the relative agreement of retention, 4% and 5%,

Table 16. Physical constants of some onion volatiles.

Compound	Molecular weight	Molecular length (Å)	Boiling point (°C)	Solubility in water
Propanal	58.08	3.08	48.8	Soluble
Propanol	60.11	3.08	97.4	Miscible
Propanethiol	76.17	4.89	67.8	Slightly soluble
Methyl propyl disulfide	122.16	8.74	--	Insoluble
Dipropyl disulfide	150.31	11.82	193.5	Insoluble

and indicates that the difference in final retention between propanol and propanethiol is mostly due to the difference in initial volatile concentration. On the other hand, the losses of dipropyl disulfide and methyl propyl disulfide are higher than expected on the basis of concentration alone. These compounds are very different from the others, as Table 16 reveals. Particularly significant would be their molecular size and limited solubility in water, which has been shown to be a critical factor (Massaldi & King, 1974a, b; Smyrl & Le Maguer, 1978).

Also to be noted in Figure 26, is the difference in rate of loss of these four particular compounds before they were locked in. Propanethiol was lost very rapidly, methyl propyl disulfide and dipropyl disulfide were lost at lower rates, and propanol was lost at an even lower rate. These differences in rates of loss can be attributed to differences in initial concentrations, differences in relative volatility of the four compounds and to their differences in affinity for water, solids and other chemicals, including volatile compounds.

The relative volatilities of propanethiol, dipropyl disulfide and 1-propanol varied appreciably (Table 14). Propanethiol, for instance, was about four thousand times more volatile than propanol and about 20 times more volatile than dipropyl disulfide. As discussed previously, according to the equation developed by Menting *et al.* (1970) with α_{io} values of the magnitude shown in table 14, drying of onion will result in

a very rapid depletion of some of the flavour components but not necessarily of others. This can be illustrated by the following example. The retention of propanethiol, a compound with very high relative volatility, would be 1.8×10^{-83}% when 1% of the water is evaporated. However, the retention of propanol, a compound with low volatility, would be 95% and 61% for 1% and 10% of the water evaporated, respectively. The Menting *et al.* (1970) equation, however, holds only if the evaporation at the surface is not limited by mass transport, and in dehydration of onion this condition can be fulfilled at the beginning of drying. Hence, at least during this phase of drying, the differences in rates of loss between onion volatiles can be partially attributed to the differences in relative volatilities of the compounds.

The lower rate of loss of propanol at higher moisture contents than at the intermediate ones appears to be due to some synthesis of this compound within the onions after the initiation of drying. This implies that, although the rate of loss of this compound is probably similar to that of the other compounds investigated, its simultaneous synthesis and loss result in the unexpected overall effect. Further work to elucidate this interaction is necessary.

Figure 27 shows dipropyl disulfide content in percent of the initial amount in drying Yellow Globe and White Globe onion as a function of drying time. As stated previously, the initial solids content of the two types of onion was 21.11% for white and 12.87% for yellow type. The ratio between the dipropyl

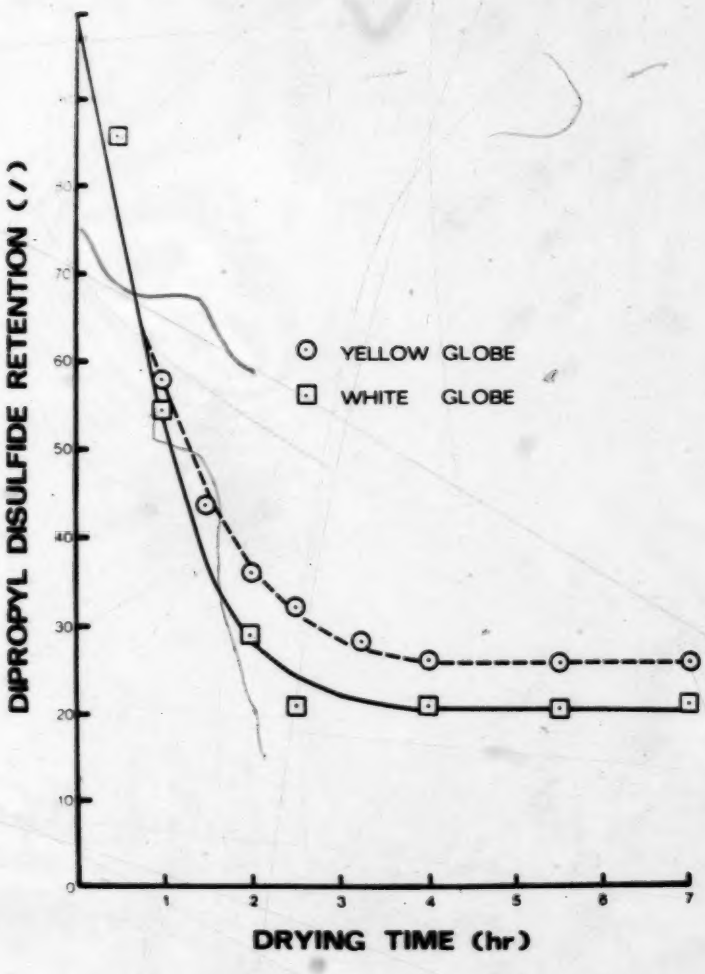


Figure 27 Dipropyl disulfide content in percent of the initial amount in drying Yellow Globe and White Globe type onions as a function of drying time. Drying conditions: 50°C and 8.1 m^3/min air flow rate.

disulfide concentration, as determined from the peak area present in the fresh white to the dipropyl disulfide concentration present in the fresh yellow onions, was 3.38. If one assumes, based on data available for sparingly soluble compounds (Smyrl & Le Maguer, 1978), that the effect of initial solids concentration on the final volatile retention is linear in this range, and that the effect of initial volatiles concentration can be predicted from the previous argument, a correction for initial solids and initial concentration would lead to a calculated value for the final retention of 23%, which compares quite favorably with the 22% observed.

The results of the microscopic analysis are shown as representative photographs in Figure 28. Figure 28(a) and 28(b) show typical longitudinal and tangential views of vascular bundle and surrounding parenchyma cells (Appendix 9). The dark area in the photographs indicates the location of the sulphur-containing volatiles which reacted with silver nitrate (Becker & Schuphan, 1975). This reaction is specific to sulfur-containing components of onion, and it results in a black silver sulfide which is practically insoluble. This was demonstrated by treating the stained onion tissue with concentrated potassium cyanide solution. It was found that there was an immediate disappearance of the black color in the cells immediately adjacent to the vascular bundles (bundle sheaths), while the outer epidermis and the parenchyma tissue, even after 6 h of treatment, retained a greyish and reddish tint, respectively.

The results of the taste panel evaluation confirmed the

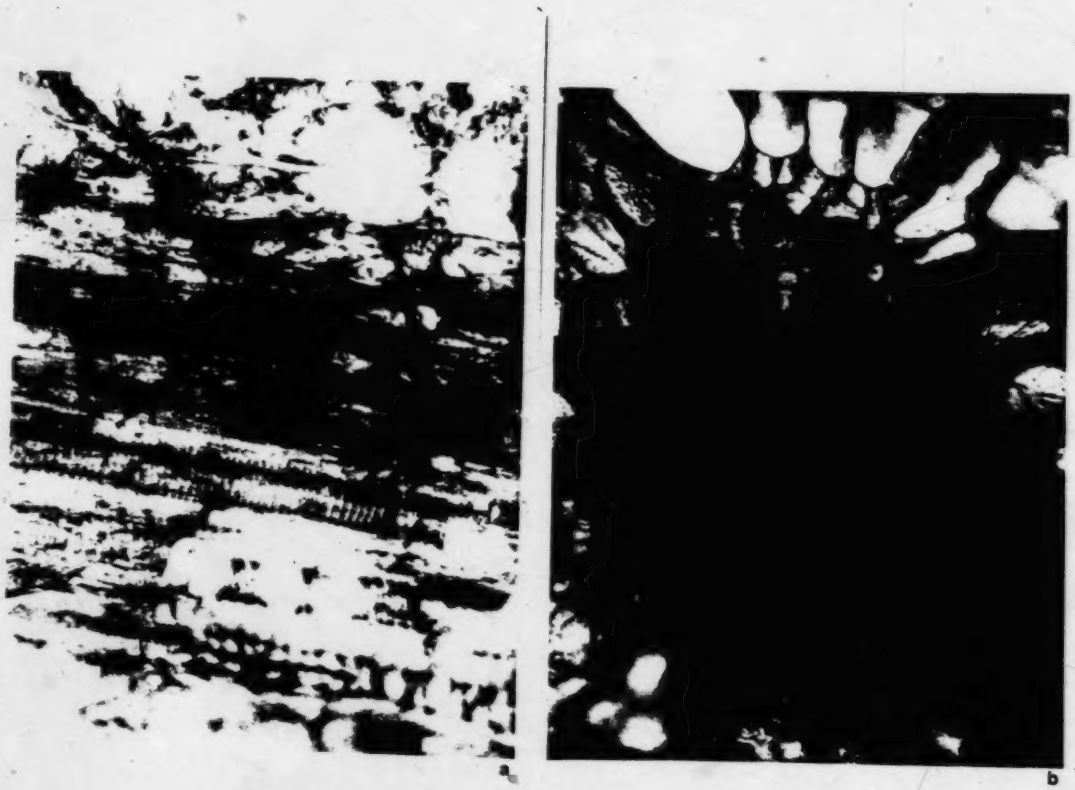


Figure 28. Cross section of ripe onion scale tissue stained with 1% aqueous silver nitrate (magnification 150X). (a) Longitudinal section through vascular bundle; (b) Tangential section of the same bundle.

microscopic observations by showing that the onion flavour was most pronounced in the section containing the vascular bundle. The section without the vascular bundle was designated as sweet, and the outer epidermis was found to be bitter.

Upon examining the photographs presented in Figure 28, from the standpoint of existing theories on volatile retention, it is apparent that the onion volatiles are located within natural microstructures, and it is probable that as drying proceeds local high solute concentration zones would form. So that one would most likely have a mechanism of volatile retention compatible with the microregion concept. On the other hand, since the cells of the bundle sheath, where the volatiles are located, are adjacent to the exylem and phloem, which are adapted to the movement of water and other plant nutrients, it is conceivable that, once drying has begun and the selective cellular transport has been disrupted, the volatiles may well tend to escape through these conductive tissues. The fact that the volatiles are not lost completely with drying indicates that selective transport across cellular elements plays a major role.

Figure 29 shows a schematic representation of a partially dried onion slice with representative aroma-containing cells. Transport of water to the surface as pointed out previously occurs in the gas phase, and it is caused by the negative concentration gradient in the direction of the surface. When the drying front reaches a cell containing aroma, it can be expected that water and aroma migrate through the cellular membrane as

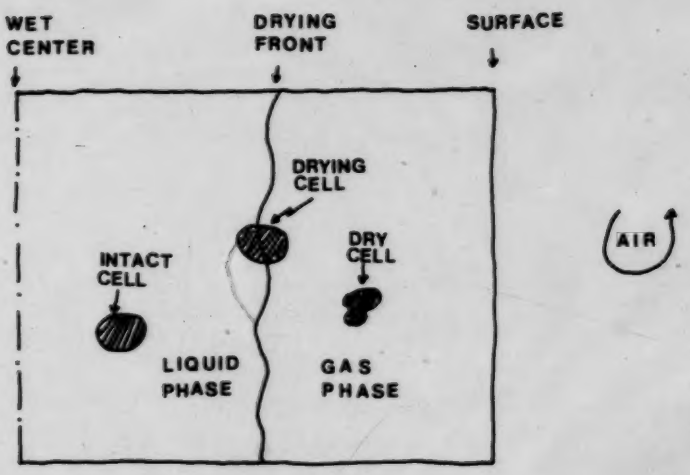


Figure 29. Schematic representation of a drying onion slice with representative aroma-containing cells.

liquids, at a rate corresponding to the cellular permeation flux, and then evaporate. From membrane permeability studies (Roman *et al.*, 1979; Rotstein & Cornish, 1978), it is known that the cellular water permeation flux is higher by several orders of magnitude than the water vapor fluxes observed in this study. Thus, there is strong indication that the drying process is controlled by resistances external to the cell. Aroma, however, is probably retained mostly within the cell. This is because, as water leaves the drying cell, the solute concentration within the cell increases, thus restricting the flow of the aroma compounds out of the cell. The quantity of aroma locked in the cell is thus dependent on the initial concentration of the volatiles, solids concentration, temperature, properties of the aroma components and properties of the cellular membrane. Small quantities of aroma may be adsorbed on the already dry layer as it migrates to the surface (Figure 29); however, the contribution of adsorption, as compared to that of entrapment, to the total amount of volatile retention is probably small.

Other workers dealing with food models (Bomben *et al.*, 1973) have observed that the ratio of the liquid diffusion coefficient of an organic component (D_i) if present at low concentration, to that of water (D) tends to decrease very sharply with decreasing water content. This implies that at low water concentration the ratio Di/D becomes so small that the system can, in fact, be considered as being permeable to water only. Thijssen (1971) reports that this selective diffusivity for water at low water concentrations is a property that all noncyrstalline hydrophilic

organic systems have in common and has called the ratio D_i/D the "selective diffusivity". According to Thijssen, the selective diffusivity is strongly dependent on temperature.

Figure 30 shows results for dipropyl disulfide retention at four dehydration temperatures as a function of moisture content. The results obtained for other volatiles with respect to temperature were similar, although not as striking. Figure 31 shows a plot of critical moisture content (the moisture content at which the aroma is locked in) as a function of temperature for dipropyl disulfide retention. It can be seen that final retention increased with increasing dehydration temperature. This can be explained by the increased solubility of the volatile with increasing temperature, which results in the maintaining of the volatile in the water phase, hence, increasing retention. Also, by increasing the temperature, the drying rate increases. This leads to a more rapid formation of the dry layer, and to a lowering of the diffusion of the flavour component at the evaporating surfaces. It is also possible that, due to the high rate of drying and the cellular nature of the material, local high solute concentration zones would form. Therefore, one would most likely have a drying process in which the selective diffusion concept and the micro-region concept would both apply.

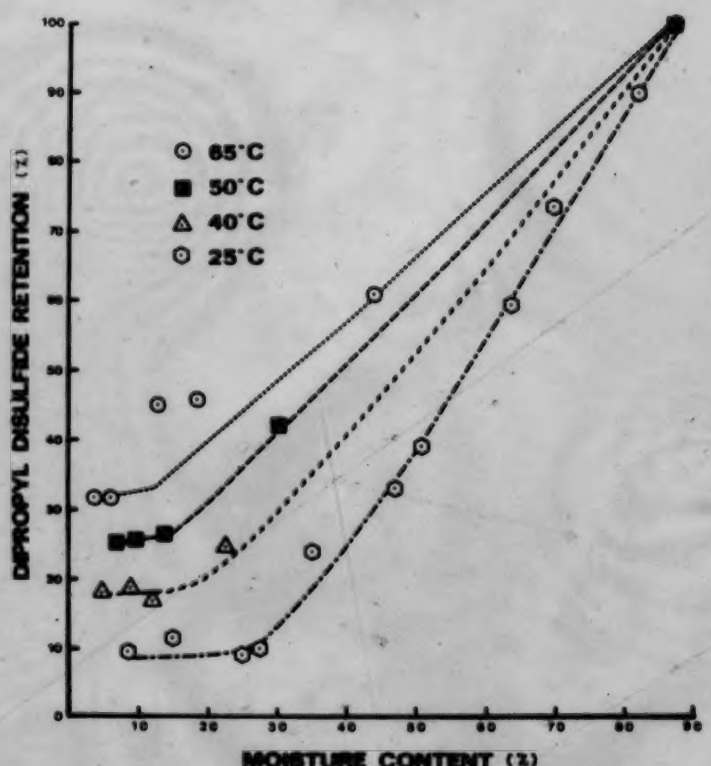


Figure 30. Dipropyl disulfide content in percent of the initial amount in drying Yellow Globe type onion, as a function of the moisture content of the onion slices dehydrated at 25, 40, 50 and 65°C, and 8.1 m^3/min drying air volumetric flow rate.

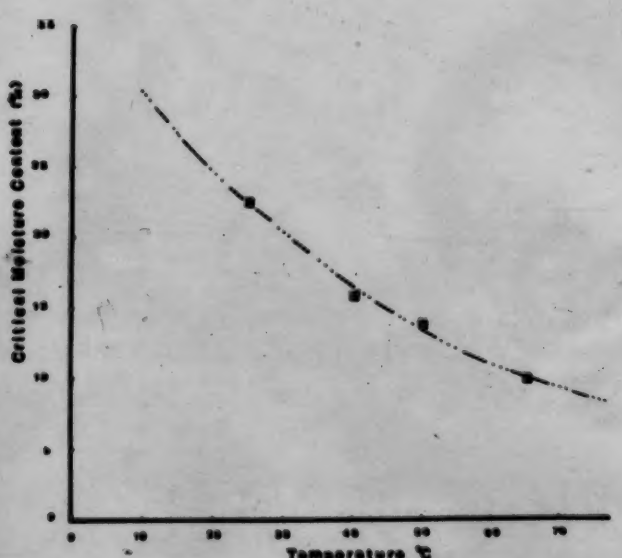


Figure 31. Effect of temperature on the critical moisture content of dipropyl disulfide retention.

5. AROMA INTENSIFICATION

5.1 Experimental

Dehydrated, chopped onions with approximately uniform final moisture contents of 9.0% and dimensions of 1.5 x 2.5 x 6.5 mm were used for this aspect of the study. The onions, cv. South Port White Globe, were grown at the Alberta Horticultural Research Center, Brooks, and dehydrated as described previously.

Gas chromatograms were made for the volatiles trapped on Tenax-GC in 15 minutes at 40°C and in 30, 60 and 120 minutes at 22°C. Samples were prepared by mixing 11.6 g of onion with either 38.4 ml of freshly boiled distilled H_2O or an equal volume of cysteine solution (1 g/L), using the method described previously. Nitrogen, at 40 ml/min, was used to continuously flush the volatiles from the sample to the Tenax trap. GC retention time data and comparison of mass spectra with standard spectra were used for the identification of some of the compounds. A Hewlett-Packard model 5710A gas chromatograph was used for the GC-MS analysis. Stainless steel columns, were used to separate the volatiles. The columns were temperature programmed for all runs. The oven was held at 60°C for 4 minutes after injection, then programmed at 4°C/min to 190°C with a final period of 24 minutes at 190°C. The flame ionization detector temperature was 250°C. Nitrogen was used as the carrier gas and the flow rate was 30 ml/min. The area of the peaks was measured with a Hewlett-Packard 3380A electronic integrator.

5.2 Results and Discussion

The chromatograms of the headspace volatiles from rehydrated onion and water, and onion and cysteine solution mixtures held at 40°C and trapped on Tenax-GC in the first 15 min of mixing are shown in Figure 32. The area under these peaks is given in Table 17. together with the Δ area and the identity of some of the compounds. The numbers shown near the peak apex in Figure 32-A, which refer to the retention time in minutes, are used in Table 17 as the peak designations. In the first 15 min at 40°C the effect of cysteine was to decrease most peaks, with the exception of dipropyl disulfide and two unknowns. Most pronounced was the decrease in propanethiol and propanal, which go from a peak area of 125.0 cm^2 to 35.5 cm^2, and from 56.21 to 10.06 cm^2, respectively. This corresponds to decreases of 71.6 and 82.1%. Dipropyl disulfide on the other hand, increased by 23.8% in the sample rehydrated with 1 g/L cysteine solution.

The difference in volatiles developed at 22°C from onion rehydrated with water and with cysteine solution is illustrated in Figure 33. The chromatograms show a varying number of peaks, 11 for the onion sample rehydrated with water for 30 min, to a maximum of 14 peaks for the sample rehydrated with cysteine solution for 120 min. The means of three replicates of the areas under these peaks are shown in Table 18 together with the percentage change in areas and the identities of the corresponding compounds. The retention times given previously in Table 17 are also used in Table 18 for peak designation.

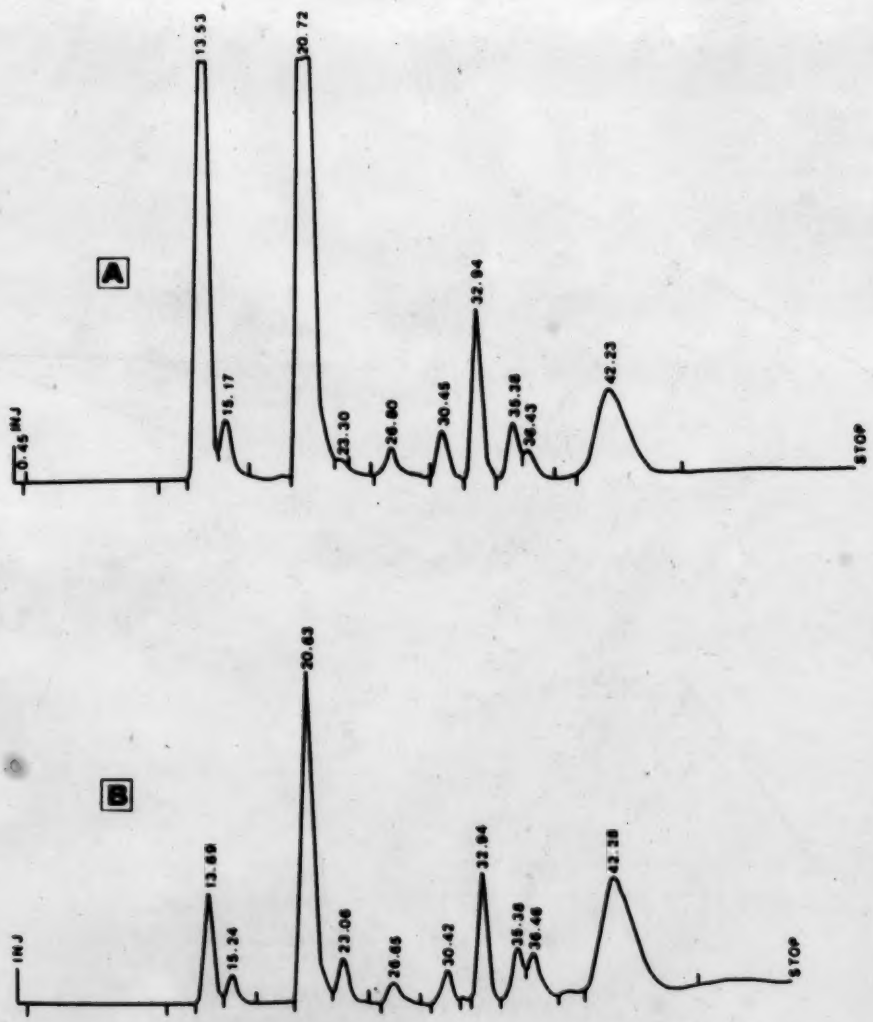


Figure 32. Gas chromatograms of headspace volatiles developed from onion at 40°C and trapped on Tenax-GC for 15 min: (A) sample rehydrated with water; (B) sample rehydrated with cysteine solution.

Table 17. GC headspace peak areas and area percent of onion rehydrated with water or cysteine solution for 15 min at 40°C.

Peak with retention time (min)	Compound	Peak area[1] (cm^2)			Area (%)	
		Water	Cysteine	Δ Area[2]	Water	Cysteine
13.53	Propanal	56.21	10.06	+ 46.15	22.92	8.89
15.17	Propanol	5.82	2.86	+ 2.96	2.37	2.53
20.72	Propanethiol	125.00	35.50	+ 89.50	50.97	31.36
23.30	Unknown	.34	4.92	- 4.58	0.14	4.35
26.80	Unknown	3.57	2.76	+ .81	1.45	2.44
30.45	2-Methyl pent-2-enal	4.91	3.28	+ 1.63	2.00	2.90
32.44	Unknown	15.92	11.72	+ 4.20	6.49	10.35
35.38	Methyl propyl disulfide	5.69	4.70	+ .99	2.32	4.35
36.43	Unknown	3.32	5.24	- 1.92	1.35	4.60
42.23	Dipropyl disulfide	24.49	32.16	- 7.67	9.98	24.41

[1] *The peak area figures are means of three replicates and the coefficient of variation was ≤ 5%.*

[2] *+ sign = water superior in volatile development*
- sign = cysteine superior in volatile development.

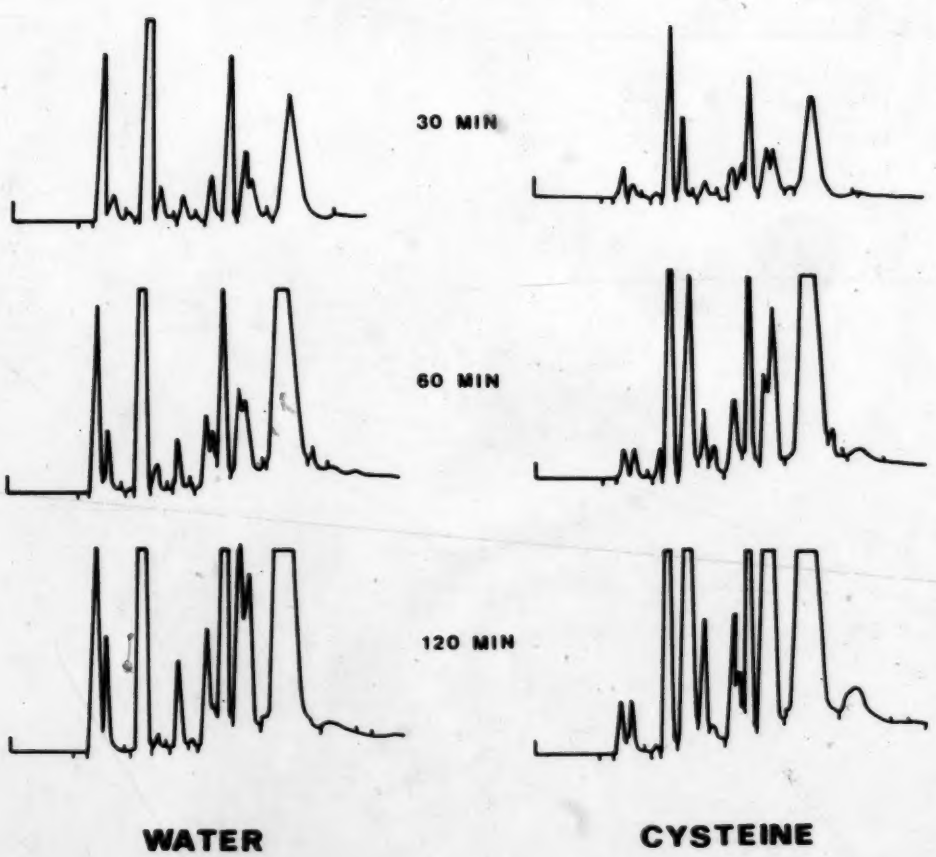


Figure 33. Gas chromatograms of headspace volatiles developed from onion at 22°C and trapped on Tenax-GC for different times.

Table 18. GC headspace peak areas of dehydrated onion volatiles developed during rehydration at 22°C with water and cysteine solution.

Peak with retention time (min)	Compound	Peak area[1] (cm^2)								
		30 min Sampling			60 min Sampling			120 min Sampling		
		Water	Cysteine	% Change[2]	Water	Cysteine	% Change	Water	Cysteine	% Change
13.53	propanal	32.60	5.08	+ 84.4[3]	35.02	5.88	+ 83.2	40.80	11.41	+ 72.0
15.17	propanol	5.53	2.44	+ 55.9	13.12	5.46	+ 50.8	25.84	12.51	+ 51.6
20.72	propanethiol	137.98	34.74	+ 74.8	226.82	59.11	+ 73.9	256.30	86.70	+ 66.2
23.30	unknown	7.64	16.22	- 52.9[3]	4.21	53.74	- 92.2	3.04	153.25	- 98.0
26.80	unknown	5.36	3.21	+ 40.1	8.87	10.51	- 15.60	17.25	27.95	- 38.3
30.45	2-methyl pent-2-enal	10.07	6.61	+ 34.4	14.42	14.09	+ 2.2	24.73	25.86	- 4.4
32.94	unknown	34.33	24.06	+ 29.9	49.24	47.30	+ 3.9	114.97	114.62	+ 0.3
35.36	methyl propyl disulfide	14.33	8.65	+ 39.6	18.61	15.58	+ 16.3	51.55	44.30	+ 14.1
36.43	unknown	9.34	11.86	- 21.2	16.97	40.01	- 57.6	43.43	87.42	- 50.3
42.23	dipropyl disulfide	71.93	56.56	+ 21.4	162.68	224.88	- 38.2	390.81	491.27	- 20.4
	Total	329.11	169.43	+ 48.5	549.56	477.56	+ 13.2	968.72	1055.29	- 8.2

[1] *The peak area figures are means of three replicates.*
[2] *Calculated as area of* ($Peak_{water}$ - $Peak_{cysteine}$) *divided by* ($Peak_{water}$) *times 100.*
[3] *+ sign = water superior in volatile development.*
- sign = cysteine superior in volatile development.

As with the samples rehydrated at 40°C for 15 min, the effect of cysteine on volatiles developed for 30 min at 22°C was to reduce the area under most peaks. The exceptions were two of the unidentified peaks, which increased. Major decreases occurred in propanal, propanethiol and propanol. Dipropyl disulfide, which has been used to assess the pungency of onion (Tewari & Bandyopadhyay, 1977), also decreased in the sample rehydrated with cysteine solution.

When sampling time was increased to 60 min, cysteine still reduced the total peak area by 13.2%, but the decrease was less than for the 30 min sampling. Propanal, propanol and propanethiol decreased by 83.2, 50.8 and 73.9%, respectively. 2-methyl pent-2-enal, methyl propyl disulfide and an unidentified peak decreased by 2.2, 16.2 and 3.9%. Most importantly, dipropyl disulfide and two unknowns increased by 38.2, 92.2 and 15.6%. After 2 h of sampling the effect of cysteine was nearly reversed. Instead of suppressing most of the peak areas, it increased them. Thus, the total area of the ten major peaks increased by 8.2%, and a new peak having a retention time of 48.97 min appeared. Its area was 4.91×10^2 cm^2 as compared to 3.98 cm^2 for the same peak in the sample rehydrated with water (see Figure 33).

Table 18 also shows that, for the lower boiling point volatiles, such as propanal and propanol, the peak area generally does not double with doubling of the sampling time. In the samples rehydrated with water, for instance, the peak area for propanal increased from 32.60 cm^2 after 30 min to only 40.80 cm^2 after 2 h. The peak area for the higher boiling point volatiles, on the other

hand, more than doubled when the sampling time was doubled. The area of the propyl disulfide peak in the sample rehydrated with water increased from 71.93 cm^2 after 30 min sampling, to 162.68 cm^2 after 60 min, and to 390.31 cm^2 after 120 min sampling. In the sample rehydrated with cysteine solution, dipropyl disulfide peak area rose from 56.56 cm^2 after 30 min, to 224.88 cm^2 after 60 min, and to 491.27 cm^2 after 120 min sampling. Similar results were obtained when volatiles of fresh onion samples were trapped for different lengths of time. Doubling of the size of the trap did not alter the results significantly.

A comparison between the results presented in Table 17 and 18 shows that volatile development was generally enhanced by temperature. The peak area for propanal, for instance, was higher for the samples held 15 min at 40°C than at 22°C for 30 min. At these two times and temperatures, the propanethiol peak had nearly the same area, while dipropyl disulfide was much higher in the samples rehydrated for 30 min.

All these results do not, by any means, alter the findings of Schwimmer & Guadagni (1967) that adding cysteine to food products prepared from onion increased their odor intensity. The present results actually confirm this, but only when at least 1 h has passed from the start of the rehydration process at 22°C. Rehydrating of onion with cysteine solution instead of water for a 30 min period will have an undesirable effect on odor intensity, as assessed by percent change in peak area [calculated as 100 x ($Peak_{water}$-$Peak_{cysteine}$) divided by $Peak_{water}$]. After 2 h of onion rehydration,

propanal, which has been suggested as an index of the lachrymatory properties of onion (Tewari & Bandyopadhyay, 1977), was 72% lower in cysteine than in water. Based on these results, it seems that the 20-fold increase in odor intensity obtained by subjective test panel judgement (Schwimmer & Guadagni, 1967) seems to correspond to our 20.4% area increase for dipropyl disulfide.

The question can be raised whether the observed cysteine effect is the result of direct influence on the enzymatic alliinase reaction, which converts non-volatile cysteine sulfoxide flavour precursors to volatiles, or is the result of a simple interchange between cysteine and the intermediate products of the enzymatic breakdown of precursors. Figure 34 shows the scheme proposed by Boelens *et al.* (1971) for formation of propanal, along with some other volatiles, following alliinase action on trans-(+)-S-(1-propenyl)-L-cysteine sulfoxide. Their scheme also involves conversion of pyruvate to aldehydes. It is not known whether enzymes are involved in some or all of these steps, but the addition of cysteine may very well alter these reactions and may result in the observed decrease in propanal peak area. Whitaker (1976) suggests that alcohols in onion may arise from the action of alcohol dehydrogenase (Alcohol: NAD oxidoreductase) on the corresponding aldehydes. If this is true, then the decrease in propanol with the addition of cysteine must be less than the decrease in propanal. As seen from Table 18, this is the case. Schwimmer & Guadagni (1967) attributed the increase in odor intensity, at least in part, to participation of cysteine in SS-SH type interchanges involving di- and mixed methyl, propyl, and propenyl

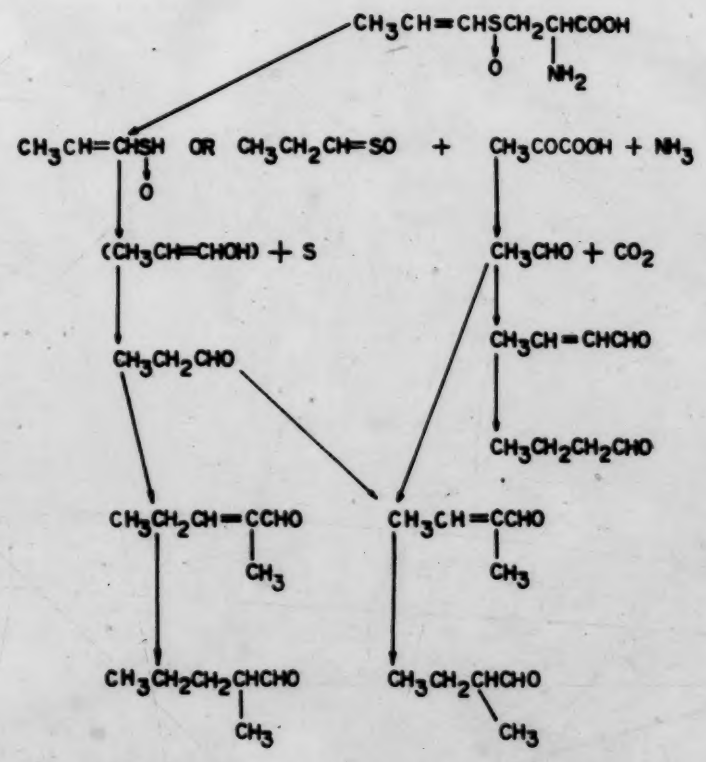


Figure 34. Formation of carbonyl compounds in onion, as proposed by Boelens *et al.* (1971).

derivatives of disulfides, trisulfides, and thiosulfinates, as well as thioaldehydes and H_2O. The mechanisms by which sulfur-containing volatiles arise from the thiosulfinates and from thiopropanal-S-oxide are not well elucidated, hence, it would be rather difficult to speculate on why, for instance, propanethiol decreased and dipropyl disulfide increased with the addition of cysteine.

IV. CONCLUSIONS AND RECOMMENDATIONS

1. Conclusions

Air drying, rehydration characteristics, and moisture sorption properties of Improved Autumn Spice onion slices were investigated. From the isotherms at 10, 30 and 45°C, monolayer sorption values, isosteric heat of sorption, spreading pressure, molar entropy and equilibrium heat of sorption were calculated, and an attempt to relate the values of these functions to the way water is bound to the solid matrix was made. This information has provided an understanding of the limiting values for the dehydration process and a better idea of the state of water in onion.

From the drying-rate curves, at different temperatures and air flow rates, effective diffusion coefficient, heat and mass transfer coefficients, Biot number, tortuosity, and the parameters α and β, which determine the degree of internal and external mass or heat transfer control, were determined. It was found that the removal of water vapor from onion slices cannot be explained in terms of a single mechanism. The reason is that there are changes in behavior depending on the rate of drying. As a result, while at high drying air temperature and flow rate the process is internal mass transfer controlled, at low drying rate it shows the influence of external heat and mass transfer resistances.

Specific gravity measurement of onion dried to different moisture contents indicated that shrinkage increased as drying progressed and at the end of dehydration it was over 89%. Rehydration rates at 25 and 40°C were also determined and found to be independent of drying conditions.

A method of analysis suitable for routine qualitative and quantitative determinations of the volatiles of fresh and processed onion was developed following a comparison of techniques for analyzing onion aroma. The retention of four onion volatiles was then studied as a function of drying rate, location of the volatiles on the onion and several physical-chemical properties of the aroma components.

The results of the study on aroma retention during dehydration revealed that aroma components are almost completely lost before the onion reaches a critical moisture content, at which point the volatiles are locked in. Accelerating the drying rate by increasing the air temperature enhanced percent volatile retention. This is consistent with both the microregion and selective diffusion concepts. On the basis of existing data obtained in model liquid foods, it was possible to explain reasonably well the behavior of similar volatile compounds as related to their initial solids and volatile concentrations. Evidence has also been presented that at the beginning of drying compounds with higher relative volatility are lost more rapidly than compounds with lower values.

A rise in pungency of dehydrated onion with addition of cysteine was obtained, and it was time and temperature dependent. However, the complexity of the reactions involved in the release of volatiles in the presence of cysteine warrants further study.

In general, it has been found that Alberta-grown onions are capable of producing acceptable dehydrated products. However, the lower dry matter content of the Yellow Globe onion as compared to the White Globe puts the dehydrator of Alberta 'Yellow' onion at a distinct economic disadvantage. Also, the well known short harvesting season and the need for

curing and storing Alberta-grown onions make onion dehydration in Alberta a distant possibility.

2. Recommendations

The amount of information developed to date and the relative success achieved indicates that this work should be continued. Further work might include:

1. Investigation of methods (infrared radiation, surface agent, laser, etc.) to speed up the formation of a selective membrane for higher retention.

2. Studies of the mechanisms of aroma transport and retention in other actual food systems and at practical conditions.

3. Measurement of diffusivity, activity coefficients, vapor pressures, and diffusion coefficients of onion and other food aroma components.

4. Investigation of methods to intensify the aroma of concentrated foods.

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Appendix 1.

Adsorption isotherms of dehydrated onion at 10, 30 and 45°C.

10°C		30°C		45°C	
a_w	X_{1-3} (kg H_2O/100 g DM)	a_w	X_{1-3} (kg H_2O/100 g DM)	a_w	X_{1-3} (kg H_2O/100 g DM)
0.14	3.03/3.13/3.10	0.11	1.61/1.60/1.84	0.11	0.61/0.64/0.63
0.24	4.80/4.99/5.00	0.32	5.64/5.73/5.84	0.23	1.66/1.63/1.67
0.33	7.00/6.90/6.93	0.52	8.99/9.14/9.15	0.31	4.20/4.08/3.99
0.53	12.0/12.0/11.9	0.75	29.3/28.9/29.2	0.51	6.40/6.41/5.89
0.68	22.5/22.1/22.3	0.86	54.1/53.9/55.1	0.75	26.2/26.5/26.7
0.75	30.3/30.8/29.7			0.82	48.3/48.6/48.5
0.89	50.3/49.4/51.8				

Appendix 2.

Desorption isotherms of dehydrated onion at 10, 20, 30 and 45°C.

10°C		20°C		30°C		45°C	
a_w	X_{1-3} (kg H_2O/100 g DM)	a_w	X_{1-3} (kg H_2O/100 g DM)	a_w	X_{1-3} (kg H_2O/100 g DM)	a_w	X_{1-3} (kg H_2O/100 g DM)
0.14	8.18, 8.10, 8.50	0.12	4.84, 4.79, 5.00	0.11	3.70, 4.16, 4.01	0.11	1.26, 1.27, 1.24
0.24	8.30, 8.40, 8.31	0.33	6.15, 6.26, 6.27	0.32	6.19, 6.19, 5.78	0.31	4.49, 4.44, 4.58
0.33	9.26, 8.60, 9.50	0.52	12.1, 11.9, 11.9	0.52	13.7, 12.8, 12.1	0.51	6.78, 6.76, 6.78
0.53	17.30, 17.7, 17.2	0.75	28.7, 28.1, 28.0	0.75	31.7, 31.6, 31.6	0.75	27.7, 27.9, 26.5
0.68	25.4, 25.1, 25.3	0.88	45.5, 45.8, 45.6	0.86	55.7, 55.4, 55.7	0.82	50.3, 50.5, 50.3
0.75	33.1, 33.3, 33.2						
0.89	61.7, 61.4, 6.15						

Appendix 3.

Sorption of water vapour by dehydrated onion (1), amorphous sucrose (2), crystalline sucrose (3), sugar fraction (4) and nonsugar fraction of onion (5) at 30°C.

a_w	X_1 (kg H_2O/ kg DM)	X_2 (kg H_2O/ kg DM)	X_3 (kg H_2O/ kg DM)	X_4 (kg H_2O/ kg DM)	X_5 (kg H_2O/ kg DM)
0.255	0.043	0.051[a]	0.008[b]	0.041	0.010
0.375	0.065	0.090	0.013	0.072	0.018
0.540	0.095	0.164	0.015	0.131	0.033

[a] *Iglesias et al. (1975).*

[b] *Loncin et al. (1968); Audu et al. (1978).*

Appendix 4.

Sorption of water vapour by dehydrated onion (1), amorphous sucrose (2), crystalline sucrose (3), sugar fraction (4) and nonsugar fraction of onion (5) at 45°C.

a_w	$X_{(1)}$ (kg H_2O/ kg DM)	$X_{(2)}$ (kg H_2O/ kg DM)	$X_{(3)}$ (kg H_2O/ kg DM)	$X_{(4)}$ (kg H_2O/ kg DM)	$X_{(5)}$ (kg H_2O/ kg DM)
0.110	0.0063	0.017[a]	0.003[b]	0.0136	0.0034
0.245	0.018	0.052	0.008	0.0416	0.0104
0.315	0.041	0.059	0.012	0.0472	0.0118

[a] *Iglesias et al. (1975).*

[b] *Loncin et al. (1968); Audu et al. (1975).*

Appendix 5.

Evaluation of D_{eff}, Biot number and Fourier number

In order to evaluate D_{eff} it is necessary to proceed as follows:

1. From the drying curve (X vs. θ) select an experimental value for X and the corresponding value for θ
2. Employing the Gurney-Lurie chart containing the parameter $k_c^* L/D_{eff} = B_i^*$ as a function of $k_c^* \theta/L$ = Fo and $(X - X_e)/(X_o - X_e)$ = y (Figure A.1 inset), obtain the values of B_i^* and Fo for the corresponding y.
3. Plot Fo vs. Bi for any given value of y (See Figure A.1)
4. Calculate the value of $k_c^* \cdot \theta/L$ = Fo for the experiment in question, and plot this value in correspondence of $1/B_i^*$. The intercept of the two lines provides the solution.

Example:

X = 4 kg H_2O kg D.M.; θ = 1440s; $k_c^* = 4.0 \times 10^{-6}$ m^2/s;

X_e = 0.0125 kg H_2O/kg D.M.; X_o = 6.77 kg H_2O/kg D.M.

Therefore

$$y = \frac{4 - 0.0125}{6.77 - 0.0125} = 0.59 \text{ kg } H_2O/\text{kg D.M.}$$

From the Gurney-Lurie chart for y = 0.59

B_i^* = 0.05, 0.10, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, ∞

Fo = 10.3, 5.1, 2.6, 1.22, 0.67, 0.41, 0.25, 0.20, 0.13

Plot Fo vs. B_i^* on 3 x 3 cycles log graph (Figure A.3.1)

$$Fo = \frac{k_c^* \cdot \theta}{L} = \frac{1}{B_i^*} = \frac{(4.0 \times 10^{-6} \times 1440)}{0.75 \times 10^{-3}} = 7.68 \cdot \frac{1}{B_i^*}$$

That is, when Fo = 7.68 B_i^* = 1 and when Fo = 0.77 B_i = 10. The two lines intercept at B_i = 56 and Fo = 0.14. But $B_i^* = k_c^* L/D_{eff}$,

$$\text{therefore } D_{eff} = \frac{4 \times 10^{-6} \cdot 0.75 \times 10^{-3}}{56} = 5.36 \times 10^{-11} \text{ m}^2/\text{s}.$$

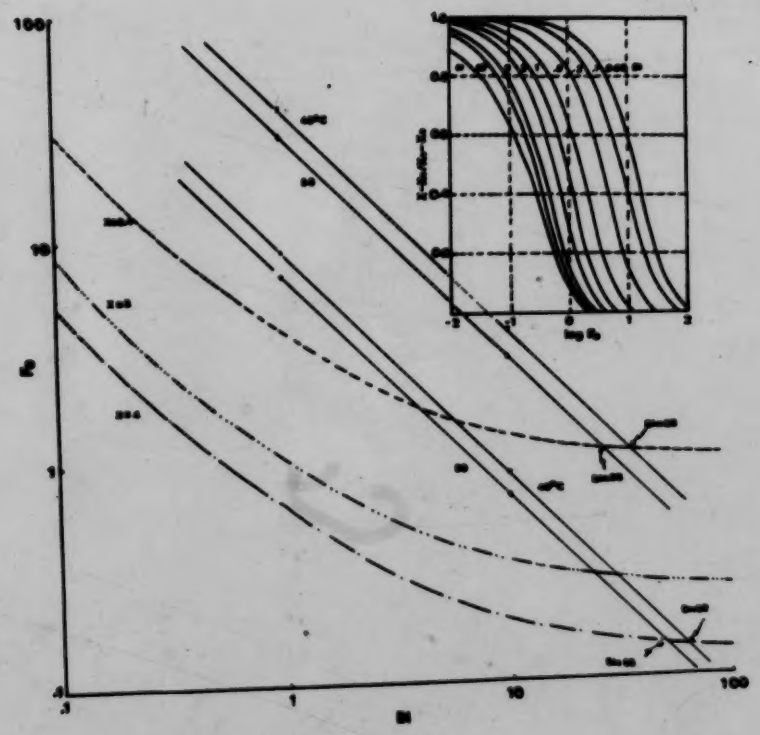

Figure A.1. Graphical method for the evaluation of D_{eff}, B_i^* and Fo. The inset was reproduced from Carslaw & Jaeger (1959).

Appendix 6.

Effect of moisture content on the specific gravity of onion slices dried at three temperatures.

kg H_2O/kg D.M.	Specific gravity (g/cc)		
	40°C	50°C	65°C
6.77	1.095 ± 0.014[a]	1.095 ± 0.014	1.095 ± 0.014
4.00	1.110 ± 0.012	1.121 ± 0.017	1.130 ± 0.011
3.00	1.115 ± 0.011	1.140 ± 0.011	1.160 ± 0.012
1.86	1.171 ± 0.010	1.185 ± 0.020	1.230 ± 0.007
1.22	1.185 ± 0.020	1.220 ± 0.008	1.260 ± 0.009
0.82	1.250 ± 0.010	1.260 ± 0.013	1.300 ± 0.020
0.54	1.290 ± 0.015	0.296 ± 0.011	1.370 ± 0.011
0.33	1.333 ± 0.017	1.331 ± 0.015	1.390 ± 0.019
0.18	1.340 ± 0.015	1.370 ± 0.020	1.421 ± 0.010
0.05	1.360 ± 0.020	1.390 ± 0.016	1.440 ± 0.025

[a] *Standard deviation.*

Appendix 7.

Calculation of shrinkage from specific gravity measurements.

1. Volume of fresh onion (V_0) = 6.77 kg H_2O + kg solid x $\frac{1}{\rho_o}$

   = 7.77 kg x 1/1.090 kg/m^3 = 7.096 m^3

2. Volume of onion at θ (V) = $\frac{X + 1}{\rho}$

3. Shrinkage (S) = $\frac{V_o - V_\infty}{V_o}$

4. $L = (\frac{V_\infty}{V_o})^{1/3} \cdot L_o$

For experiment at 40°C and 8.1 m^3/min air flow rate

V_o = 7.096 m^3, $V_\infty = 1/\rho_\infty$ = 1/1.360 = 0.375 m^3;

$S = \frac{(7.096 - 0.735)}{7.096} \cdot 100 = 89.6\%$

$(\frac{V}{V_o})_e$ = 0.735/7,096 = 0.104 m^3.

Appendix 8.

Derivation of Equation (7)

Approach 1

By definition, y, the mole fraction in the gas phase, equals the product of x, the mole fraction in the liquid phase, and a coefficient, k. If y_i is the mole fraction of a volatile, i, in the gas phase, and x_i, the mole fraction of i in the liquid phase, and if y_o and x_o denote the mole fractions of water in the gas and liquid phase, respectively, the relative volatility, α_{io}, is defined by $\alpha_{io} = k_i/k_o$.

If the total volume of the headspace system used in this work is denoted by V_T and the volume of the space occupied by the gas and liquid phases by V_G and V_L, respectively, and if it is assumed that the total pressure, P_T, equals the sum of the atmospheric pressure, Po, and the saturation pressure of pure water, P_W^S, it follows that $V_T = V_G + V_L$ and $P_T = P_o + P_W^S$. As half of the system was liquid and half vapor, $V_L = V_G + \frac{1}{2}V_T$.

The injection of known volumes of liquid, v_L, and vapor, v_G, phases in the GC unit results in a peak area, A_L, for i in the liquid phase, and a peak area, A_G, for i in the gas phase. The mass of i in the gas phase, m_G^i, is equal to kA_G, and the mass of i in the liquid phase, m_L^i, is equal to kA_L. From this it follows that the concentration of i in the gas phase, C_G^i, is equal to kA_G/v_G and the concentration in the liquid phase C_L^i, is equal to kA_L/v_L kg/m^3. Consequently, the mass of i in the gas phase equals the product of C_G^i and V_G and the mass of i in the liquid phase equals the product of C_L^i and V_L. The number of moles of i in V_G, n_G^i, equals m_G^i/M_i, and that in V_L, n_L^i equals m_L^i/M_i where M_i is the molecular weight of i.

The concentration of the volatile, i, in the solutions was very small (5 - 500 ppm), hence, if it is neglected, the number of moles of water in the solution, n_L^o, equals $V_L \rho_W / M_W$, where ρ_W and M_W are the density and molecular weight of water, respectively. The total number of moles of i and o in the gas phase, n_G^T, equals $P_T V_G / RT$, where P_T is in Pa, V_G in m^3, $R = 8.314 \times 10^3$ J/K kmole, and T is in K. The mole fraction of volatile i in the gas phase, y_i, equals n_G^i / n_G^T and the mole fraction of i in the liquid phase, x_i, equals n_L^i / m_L^o. Also, y_o equals P_W^S / P_T and $x_o \simeq 1$. Substituting,

$$k_i = \frac{y_i}{x_i} = \frac{n_G^i}{n_G^T} \cdot \frac{n_L^o}{n_L^i} = \left(\frac{A_G}{v_G} \cdot \frac{v_L}{A_L}\right) \cdot \frac{RT \rho_W}{M_W P_T} \qquad (A.1)$$

$$k_o = \frac{y_o}{x_o} = \frac{P_W^S}{P_T} \qquad (A.2)$$

$$\alpha_{io} = \frac{k_i}{k_o} = \left(\frac{A_G}{v_G} \cdot \frac{v_L}{A_L}\right) \cdot \frac{RT \rho_W}{M_W P_W^S} \qquad (A.3)$$

But if it is assumed that the water vapor follows the gas law, the density of water vapor at T, ρ_W^G, equals $M_W \cdot (P_W^S / RT)$; the term $RT \rho_W / M_W P_W^S = \rho_W^L / \rho_W^G$ and at 25°C $\alpha_{io} = k \cdot 4.333 \times 10^4$.

Approach 2

If the vapor concentrations of a volatile, i, when dissolved in water, are denoted by $[i]_v$ and $[H_2O]_v$, and if $[i]_L$ and $[H_2O]_L$ denote the corresponding liquid concentrations, and M_i and M_w denotes the molecular weight of i and water, respectively, the mole fraction of i in the vapor phase equals $([i]_v/M_i)/([i]_v/M_i) + ([H_2O]_v/M_w)$ and the mole fraction of i in the liquid phase equals $([i]_L/M_i)/([i]_L/M_i) + ([H_2O]_L/M_w$. The ratio of mole fractions (liquid/vapor) equals $([i]_v/M_i) \cdot (M_i/[i]_L) \cdot \left\{ \cdot [([i]/M_i) + ([H_2O]_L/18)]/[([i]_v/M_i) + ([H_2O]_v/18)] \right\}$

The concentration of the volatile, $[i]_L$, in the solution was very small, compared to the concentration of water $[H_2O]_L$ hence if it is neglected, the concentration of water $[H_2O]_L$ equals 1000 g/L.. Therefore, if the ratio is denoted by α_{io};

$$\alpha_{io} = \frac{[i]_L}{[i]_L} \frac{[H_2O]_L/18}{([i]_v/M_i) + [H_2O]_v/18} = \frac{[i]_L}{[i]_L} \cdot \frac{1000}{18} \cdot \frac{1}{([i]_v/M_i) + ([H_2O]_v/18} \qquad (A.4)$$

if $[i]_v$ is small compared $[H_2O]_v$

$$\alpha_{io} = \frac{[i]_L}{[i]_L} \cdot \frac{1000}{[H_2O]_v} \qquad (A.5)$$

and, as at 25°C 1 liter of air saturated with H_2O contains 2.305×10^{-2} g of H_2O, $\alpha_{io} = k \cdot 4.333 \times 10^4$.

Appendix 9.

Morphology and Histology of Onion

The onion bulb consists of several white, fleshy, modified leaf bases or scales surrounding by pigmented membranous scales. All the scales form complete layers, appearing as concentric rings in cross sections (Figure A. 2-B). The outer scales are dry and papery, consequently, inedible; the inner scales, thick and fleshy. There are white, yellow and red varieties, the color being chiefly in the dry scales and outer fleshy scales.

The scales are made up of an outer epidermis, several layers of mesophyll parenchyma cells, vascular tissue with spiral vessels, and an inner epidermis. In the subepidermal cells of the dry scales, single prismatic crystals of calcium oxalate, reaching 50 μ in length occur (Parry, 1969). These crystals are a metabolic end-product and are seldom found in the fleshy scales of mature onion. The latex tubes or ducts (Figure A. 2-C) containing a milky fluid occur at intervals between the subepidermis and the mesophyll. Strictly speaking, they are not tubes but large sacs arranged end to end. They are forms of excretory or secretory cells, the latex being the extruded material. The tubes are single and distributed at regular distances usually separated by 2 to 4 parenchyma cells. The mesophyll, which, with the exception of the vascular bundles, includes all the cells between the outer and inner epidermis, is composed of thin-walled cells with living protoplasm and a nucleus. The fibro-vascular bundles occur in the inner part of the mesophyll, and have conduction and support functions. They are composed of two kinds of tissue of fundamental importance, xylem and phloem. The

xylem and phloem are composed of elongated cells (Figure A.2-G). adapted to the movement of materials throughout the plant. The four principal types of cells in xylem are fibres, tracheids, vessels and parenchyma. Tracheids and vessels conduct water and also contribute to the mechanical strength of the xylem (Cutter, 1969). Fibres are involved in mechanical support only. Parenchyma cells function in storage and lateral transport. In onion the vessels are largely spiral with variable bands. Annular and reticulated vessels are also present. The most important conducting cells of the phloem are the sieve-tube elements, so called because of the presence of sieve-like openings in the end and frequently on the side walls. The vascular bundles are surrounded by a tight sheath of parenchyma cells, the bundle sheath (Figure A. 2-D and A.2-G) The cells of the sheath in onion are elongated parallel to the veins and have living protoplasm and thin walls. Inter-cellular spaces are lacking between the cells of the sheath and between these and the enclosed vascular bundle. The sheath cells are in intimate contact with the mesophyl cells, and all the materials moving from or into the vascular bundles must pass through this sheath (Wilson & Loomis, 1967).

There are indications that the onion volatiles precursors, trans-(+)-S-(1-propenyl)-L-cysteine sulfoxide, (+)-S-methyl-L-cystein sulfoxide and (+)-S-propyl-L-cysteine sulfoxide, are located in the latex tubes (Rendle, 1889). However, according to Helm (1956) the oil is present in the epidermic cells and vascular bundle cells.

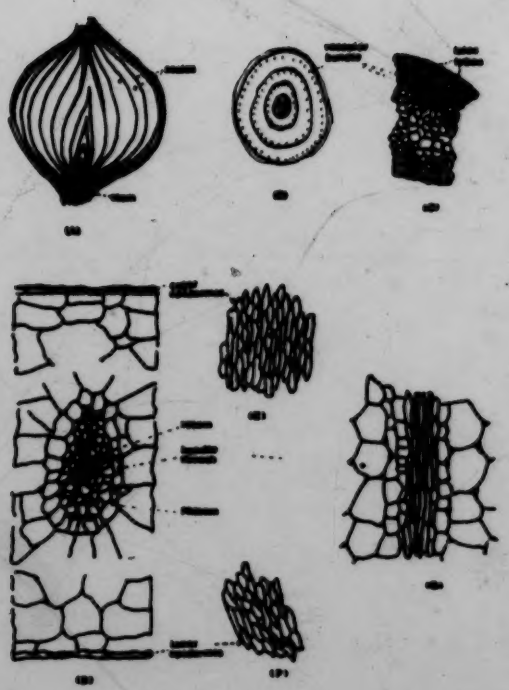

Figure A.2. Onion bulb sections with zones of tissue designation pertinent to the present study. (A) Longitudinal section of bulb. (B) Cross section of bulb. (C) Cross section of scale. (D) Cross section through a scale vascular bundle. (E) Surface view of outer epidermis. (F) Surface view of inner epidermis. (G) Longitudinal section of vascular bundle.

VITA

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Number of Children: Two

Present Status: Canadian Citizen

Academic

Degree	Subject	Institution	Year Started	Year Finished
Ph.D.	Food Processing	University of Alberta, Edmonton, Alberta	1976	1980
M.Sc.	Food Science	University of Manitoba, Winnipeg, Manitoba	1972	1973
B.Sc.A.	Food Science	University of Manitoba; Winnipeg, Manitoba	1968	1972
Dip. Agr.	General Agriculture	Technical Institute for Agriculture, Lavello, Italy	1962	1967

Research and Working Experiences

Period	Institution/Company	Responsibilities	Position
Jan., 1975 to date	Alberta Horticultural Research Center, Brooks, Alberta	Identification, initiation, supervision & coordination of food processing related projects with the end result being to provide assistance to Alberta's food processing industry in helping to maintain & expand its domestic & export market share.	Scientist

Sept., 1976 June, 1980	The University of Alberta, Edmonton	A study of dehydration and aroma retention in onion	Graduate Student
Sept., 1973 Jan., 1975	Burns Foods Ltd., Winnipeg & Calgary	Production control of meat & fruit & vegetable products	Management Trainee - Assistant Provision Manager
Apr., 1972- Sept.,1973	The University of Manitoba, Winnipeg	Treatability study of waste water from fresh water fish processing plants.	Graduate Student
Apt., 1972- Sept., 1972	The University of Manitoba, Winnipeg, E.P.A. Corvallis, Oregon; National Canners Assn., Berkeley, Cal.	Collect published information on water use in the food processing industry	Summer Student
Apr., 1971- Sept., 1971	Manitoba Dept. of Agriculture Pesticide Residues Unit	Analyze milk and milk products for pesticides.	Summer Student

Awards/Distinction

1. Dean's honor list for outstanding grade point average in first year Agriculture, University of Manitoba, Winnipeg.

2. Gold Medal for standing first in order of merit in Dip. Agr. final examination in 1967, Istituto Tecnico Agrario Statale, Lavello, Italy.

Membership in Societies/Committees

1. Member of the Canadian Institute of Food Science and Technology - 1973 - to date.

2. Member of the American Institute of Food Technologists - 1976 - to date.

3. Member of the Potato Association of America - 1976 - to date.

4. Member of the Alberta Food Processing Industry Advisory Council - 1975 - to date.

5. Member of N.A.I.T. Industrial Food Technology Advisory Committee - 1975 - to date.

6. Member of the Alberta Institute of Agrologists - 1978 - to date.

Languages

Language	Speaking	Reading	Writing
English	Good	Good	Good
Italian	Good	Good	Good
French	Some	Fair	Some
Spanish	Some	Some	--

List of Courses Taken at Universities

Ph.D. Introduction to Food Engineering 383, Food Engineering Lab 587, Chemical Engineering 502 (Proc. Dsgn Poll. Cont) (Audit), Food Science Seminar 600, Topics in Food Science 601, Chemical Kinetics 573 (Audit).

M.Sc. Food Research 424, Food Additives 708, Water and Waste 706, Grad Seminar 702, Waste Management 705, Agric. Marketing 204, Food Plant Mechanics 401.

B.S.A. Organic Chem 122, Math, Calculus 136, Math, Linear Algebra 137, Economics 120, Agriculture 105, Biology 125, Microbiology 220, Psychology 120, Physical Chemistry 120, Animal Science 202, Crop Science 207, Soil Science 202, Genetics 202, Food Science 314, Food Processing 315, Computer Science 120, Food and Nutrition 203, Anatomy and Physiology of Insects 312, Macroeconomics Theory 230, Geography 120, Food Science 412, Food Problems 414, Food Microbiology 415, Food Analysis 416, Quality Control 420, Food Chemistry 421, Food Chemistry 422, Statistics 221.

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Mazza, G. and Co-Workers. Food Processing and Quality Evaluation Program at the Alberta Horticultural Research Center. (Reports on several activities) 1979, 1978, 1977, 1976 and 1975 A.H.R.C. Annual Reports.

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